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MULTI-ELEMENTAL ANALYSIS AND POTENTIAL HUMAN HEALTH RISK ASSESSMENT OF SELECTED CANNED FOODS SOLD IN NIGERIA

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Abstract: *This study was aimed at analysing multi-elemental levels (Al, Bi, Ca, Fe, K, Li, Mg, Mn, Na, Si, Sr, Th, and Zn) and potential human health (estimated daily intake and non-carcinogenic) risk impact of canned foods (soya beans and Sardine) sold in Swali markets. Using Inductively coupled plasma atomic emission spectroscopy (ICP-OES) techniques. The results reveal the presence of Al, Bi, Ca, Fe, K, Li, Mg, Mn, Na, Si, Sr, Th, and Zn in the two canned food samples. The order of the element's concentration of the soya beans sample in the study was K>Ca>Fe>Mg>Na>Si>Li>Th>Al>Mn>Sr>Bi>Zn, while for canned sardine sample was K>Ca>Fe>Mg>Na>Si>Al>Th>Li>Bi>Mn>Sr. The concentration levels of all detected components were found to be significantly low, much below the maximum limits established by the Codex Alimentarius Commission, Food and Agriculture Organization, and World Health Organization. The non-carcinogenic risks of the food samples were assessed by calculating the estimated daily intake (EDI), Target Hazard Quotients (THQ), and Hazard Index (HI). The evaluation of the soya beans and sardine samples revealed that the human health risk associated with their ingestion was below permissible limits and less than 1. This implies that their level of safety to humans is high and may not constitute a threat to human health. However, it is important to continuously monitor these products and their consumption since they are widely consumed.*

Keywords: *Soya beans, Sardine, Heavy metals, Carcinogenic risk, Non-carcinogenic risk.*

1. Introduction

The continuous release of heavy metals from various sources leads to an accumulation of these substances in the environment, hence amplifying their potential hazards to human health. As stated by Kowalska et al. [1], heavy elements constitute a substantial source of environmental pollution. Certain elements are essential and indicate polluted substances due to their substantial adverse impacts, whereas others are nonessential, naturally present in low amounts, and are considered vital for many biological activities. These substances are considered highly hazardous to the environment, even in little amounts, because they are soluble and can be absorbed by organisms through many means such as air, drinking water, food, canned goods, and other synthetic chemicals and products. Their accumulation takes place gradually and progressively in the tissues of organisms, leading to various detrimental effects on these tissues [2]. Heavy metal molecules are considered the most dangerous deposited molecules since they have the ability to accumulate in the body after entering. Lead (Pb) has a higher propensity to enter the body compared to cadmium (Cd) due to its greater absorption by plants and subsequent transportation to fruits [3, 4].

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Food is a primary source of heavy metal exposure for many individuals, and recent studies are focused on implementing suitable techniques to quantify the levels of food contamination by these substances [5]. Metal contamination in food may be increasing as a result of manufacturing procedures, equipment utilized throughout the process, packing, and storage [6].

In the food industry, numerous processes are employed to generate products with varying shelf life. Canned foods have a long shelf life, do not require refrigeration, and require no special handling during shipment or distribution [1]. According to Kapica and Weiss [7], canned foods refer to products that are packaged in metal cans, glass jars, or plastic containers. The pasteurization procedure and the airtightness of the packaging preserve their extended shelf life by preventing contaminants and air from entering and contaminating the food. Some canned foods also contain chemical preservatives, such as sodium nitrate or potassium nitrate. Furthermore, it was underscored that canned food products can contain chemical pollutants, primarily originating from the environment, as well as from improper technological processing or erroneous packaging, irrespective of their taste and nutritional composition. Although employing suitable industrial and agricultural methods in food production, it is impossible to entirely eradicate the existence of chemical contaminants in food caused by environmental contamination. Heavy metals, together with other contaminants, pose a significant risk to human health [8].

People in many parts of the world like and consume canned goods because they are inexpensive and readily available. The packaging procedure aims to preserve food as fresh as possible for as long as feasible, but as the industry grows in popularity, so does the amount of cheating [9]. According to Suaad et al. [10], although the legislation from the WHO / FAO committee requires that the raw materials used in this industry be of high quality and free from defects, there is a significant lack of quality control in the local markets, leading to the presence of numerous canned foods that do not meet the legal and health standards. The presence of heavy metals in certain meals can indirectly affect consumers' health due to their deposition. The objective of this research is to examine the elemental composition of canned soybeans and sardines using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-OES) techniques.

2. Materials and methods

2.1 Materials

2.1.1 Sample collection and digestion

Canned foods (Soyabeans and Sardine fish) samples were bought from Swali markets, Bayelsa State, Nigeria. The samples were blended, tagged, and stored at -20ºC until analyzed. The microwave digestion vessel was used to directly weigh 0.5 g of solid sample and 1.0 g of liquid sample for digestion. Subsequently, 7.0mL of concentrated nitric acid (with a concentration of 70%) and 1.0mL of hydrogen peroxide (with a concentration of 30%) were introduced and subjected to digestion using a microwave system manufactured by Analytik Jena, Germany. The process of digestion was started by gradually raising the temperature over a period of 60 minutes. The program commenced at a temperature of 20ºC, ascended to 80ºC within a span of 5 minutes, subsequently dropped down to 50ºC over a duration of 15 minutes, and finally elevated to 190ºC for a period of 20 minutes. Once the contents of the tubes had cooled to the surrounding temperature, they were moved to 50 ml polypropylene bottles and mixed with ultrapure deionized water [11] until the total volume reached 20 ml. Control blanks were generated using ultrapure deionized water instead of the sample, using the same procedure as the samples. These blanks were repeatedly analyzed alongside the samples to detect any potential cross-contamination [12].

2.1.2 Chemicals and reagents

Synlab Nigeria reference laboratory in Lagos, Nigeria provided nitric acid (70%), hydrogen peroxide (30%), and ultrapure deionized water (18.2 MΩ). A 10 mg/l multielement standard solution was utilized for calibration curves. Decontamination was performed on all laboratory equipment that had been in contact with the substances by submerging it in 10% aqueous nitric acid for a duration of 24 hours, followed by a comprehensive washing with deionized water.

2.2 Method

2.2.1 Instrumental analysis

The sample digesting process utilized a Multiwave 3000 microwave combustion apparatus manufactured by Anton Paar (GmbH, Graz, Austria). This device is equipped with 20 high-pressure polytetrafluoroethylene (MF 100) digestion tubes and is capable of being programmed for both time and power settings ranging from 600 to 1400 watts. An inductively coupled plasma—optical emission spectrometer (ICP-OES) was used for macroelemental analysis. This instrument measured the concentrations of Na, K, Mg, Si, Ca, Fe, Bi, Sr, Th, Mn, Al, Li, and Zn. The Varian Model 730-ES CCD (charge-coupled device) from Wyndmoor, PA was utilized. The correction wavelength was determined manually by scanning a blank, a reference solution, and a sample solution within the programmed wavelength range. The determination was made at an appropriate background to ensure accurate measurement of the analyte peak.

A Perkin-Elmer SCIEX Elan DRC III inductively coupled plasma—mass spectrometer (ICP-MS) located in Norwalk, CT was utilized to quantify the quantities of 13 trace elements, such as Si, Fe, Bi, Sr, Th, Mn, Li, and Zn. The device was used in combination with a high-efficiency sample introduction and desolvating system, which incorporated a quartz cyclonic spray chamber. Argon gas with a spectral purity of 99.9998% was utilized. A 730-ES simultaneous charge-coupled device (CCD) manufactured by Varian in Wyndmoor, PA was utilized to ascertain the levels of Macronutrient elements, specifically Calcium (Ca), Potassium (K), Magnesium (Mg), Aluminum (Al), and Sodium (Na). The samples were quantitatively examined using the external calibration technique. The 10 ml multi-elemental standard solution was diluted with nitric acid at a concentration of 24.5%, which is equivalent to the concentration in the digested samples. Curves were generated for each analyte using eight concentrations to ensure that the content of all analytes in the samples fell within the linear dynamic range.

2.2.2 Method validation

Several quality assurance factors were tested to confirm the analytical approach used to determine trace elements in canned goods. The correlation coefficient obtained from the calibration curves of the analytes was utilized to determine the linear dynamic range by the application of nonweighted least-squares linear regression analysis. The limits of detection and quantification were determined by dividing three and ten times the standard deviation of a blank by the slope of the analytical curve [13].

The precision was determined by dividing the relative standard deviation of 10 replicates of a single sample by the coefficient of variation. The analytes were subjected to spiking at volumes of 10 and 100 ml from a standard solution. The resulting % recovery was reported to assess any experimental loss or gain during the study. The accuracy of an oyster tissue certified reference material (NIST CRM 1566b) was evaluated using the identical approach as previously reported. The estimated values were compared to the certified values [14, 15].

2.3 Human Health Risk Assessment

Equation 1 was used to calculate the Estimated Daily Intake (EDI) of toxic metals, Target Hazard Quotient (THQ), and Hazard Index (HI). These calculations were performed to assess the potential health risks to humans from consuming elements found in canned food samples, specifically Soyabeans and Sardine.

Estimated Daily Intake (EDI)

$$EDI = \frac{CMetal \times DCanned\ food\ intake}{Bwaverage} \quad (1)$$

Where:
CMetal is the metal concentration in the canned food samples in mg/kg,
DCanned food samples *intake* is the daily intake of soyabeans and sardines in kg/person and
BWaverage is average body weight in kg/person
In this study, an average daily intake of canned foods of 3.6 kg was used. In this study, an average adult body weight of 60 kg was used [16].
Non-carcinogenic health effect

THQ (target hazard quotient): THQ values were used to estimate the non-carcinogenic risk of hazardous metals ingestion. THQ is a ratio of a toxicant's determined dose to a hazardous reference dose. A vulnerable population is at danger if the ratio is equal to or greater than one. Equation 2 was used to compute THQ values [17-19].

$$THQ = \frac{Efr \times ED \times FIR \times C}{RfDo \times BWaverage \times ATn} \times 10^{-3} \quad (2)$$

Where:
Efr represents the frequency of exposure during a period of 190 days per year.
ED represents the length of exposure, which is similar to an average lifetime of 56 years.
FIR is the average daily intake in kilograms per person per day.
The variable C represents the concentration of components in canned food samples, measured in milligrams per kilogram (mg/kg).
The term BWaverage refers to the average body weight, as defined by equation (1).
RfDo stands for reference dose, which is measured in milligrams per kilogram per day.
ATn represents the average exposure time for non-carcinogens, calculated by multiplying 190 by 56. The reference doses employed were as follows: Cu = 0.040 mg/kg, Ni = 0.020mg/kg, Cr = 0.5 mg/kg, Mn = 0.014 mg/kg, Zn = 0.300 mg/kg, and Fe = 0.700 mg/kg [20, 21].
Calculation of the hazard index (HI): The hazard index is employed to evaluate the potential risk to human health in situations where many hazardous metals are concurrently present. The hazard index was calculated by summing the target hazard quotients (THQs) [22]. Given that several pollutants might result in similar adverse health effects, it is often suitable to combine THQs (Toxic Hazard Quotients) associated with multiple contaminants, as demonstrated in equation 3.

$$HI = \Sigma THQs \quad (3)$$

2.4 Statistical analysis

Using model 20 of the Statistical Package for the Social Sciences (SPSS), the data were presented as the mean ± standard deviation of triplicate measurements.

3. Results and discussion

3.1 Multi-elemental levels

The mean value of Al in canned sardine in this study (0.17±0.08 mg/l) was higher than Soyabean sample of 0.04±0.02 mg/l. The results of activity concentrations in the canned Sardine and soyabeans samples for natural radionuclides such as ^{232}Th, ^{90}Sr and ^{40}K are given in Tables 1 and 2. The highest concentrations displayed in this study in corresponded to the naturally occurring radionuclide ^{40}K. ^{40}K was found to contribute the highest activity in all the Canned food samples. The mean values of calcium, bismuth, lithium, magnesium, sodium and silicon were all below CAC/FAO/WHO maximum permissible limits as stated in Tables 1 and 2.

Table 1:
Multi-Elements concentration (mg/l) in Soyabeans Samples sold in Nigeria.

Sample	Elements (mg/l)												
Soya-beans	Al	Bi	Ca	Fe	K	Li	Mn	Na	Si	Sr	Th	Zn	Mg
	0.0492 ± 0.02	0.009 ± 0.009	3.86 ± 0.29	3.01 ± 0.01	49.8 ± 0.12	0.10 ± 0.001	0.02 ± 0.002	1.50 ± 0.01	0.47 ± 0.003	0.02 ± 0.00	0.051 ± 0.03	0.003 ± 0.00	2.91 ± 0.012
CAC/FAO/WHO	7.0	0.5	500	5	3500	-	3.0	5	-	0.02	0.01	3.00	380

Key: (Data are in Mean±SD of triplicate determination), CAC- Codex Alimentarius Commission, FAO- Food and Agriculture Organization, WHO- World Health Organization, Al: Aluminum, Bi: Bismuth, Ca: Calcium, Fe: Iron, K: Potassium, Li: lithium, Mn: Manganese, Na: Sodium, Si: Silicon, Sr: Strontium, Th: Thorium, Zn: Zinc, Mg: Magnesium

Table 2:
Multi-Elements concentration (mg/l) in Canned Sardine Fish samples sold in Nigeria

Sample	Elements (mg/l)											
Canned Sardine fish	Al	Bi	Ca	Fe	K	Li	Mn	Na	Si	Sr	Th	Mg
	0.17 ± 0.08	0.02 ± 0.01	3.24 ± 0.05	3.21 ± 0.03	42.0 ± 0.69	0.11 ± 0.001	0.014 ± 0.003	0.93 ± 0.04	0.49 ± 0.08	0.013 ± 0.00	0.17 ± 0.04	2.59 ± 0.02
CAC/FAO/WHO	7.0	0.5	500	5	3500	-	3.0	5	-	0.02	0.01	380

Key: (Data are in Mean±SD of triplicate determination), CAC- Codex Alimentarius Commission, FAO- Food and Agriculture Organization, WHO- World Health Organization, Al: Aluminum, Bi: Bismuth, Ca: Calcium, Fe: Iron, K: Potassium, Li: lithium, Mn: Manganese, Na: Sodium, Si: Silicon, Sr: Strontium, Th: Thorium, Mg: Magnesium.

Table 3:
Estimated Daily Intake (EDI) of elements for adult from ingestion of Canned Soyabeans and Sardine Fish samples sold in Nigeria.

Samples	**Elements**												
	Al	**Bi**	**Ca**	**Fe**	**K**	**Li**	**Mg**	**Mn**	**Na**	**Si**	**Sr**	**Th**	**Zn**
Soya-beans	1.6E^{-5}	3.75E^{-6}	0.0016	0.0013	0.0208	4.1E^{-5}	8.3E^{-6}	8.3E^{-6}	0.00063	0.00016	8.3E^{-6}	2.1E^{-5}	1.25E^{-6}
Sardine fish	0.000595	7E^{-5}	0.01134	0.01124	0.147	0.000385	0.00906	4.9E^{-5}	0.00326	0.00172	4.5E^{-5}	0.00059	-

Table 4:
Target hazard quotient (THQ) and hazard index (HI) for adult from ingestion of Canned Soyabeans and Sardine Fish samples sold in Nigeria

Samples	THQ													HI
	Elements													
	Al	**Bi**	**Ca**	**Fe**	**K**	**Li**	**Mg**	**Mn**	**Na**	**Si**	**Sr**	**Th**	**Zn**	
Soyabeans	$1.1E^{-8}$	$5.6E^{-12}$	$1.0E^{-6}$	$6.5E^{-7}$	0.00017	$6.9E^{-10}$	$2.7E^{-11}$	$2.7E^{-11}$	$1.57E^{-7}$	$1.1E^{-8}$	$2.8E^{-11}$	$1.75E^{-10}$	$6.3E^{-13}$	0.000172
Sardine fish	$1.69E^{-8}$	$2.33E^{-10}$	$6.1E^{-6}$	$6.E^{-6}$	0.00103	$7.1E^{-9}$	$3.9E^{-6}$	$1.1E^{-10}$	$5.1E^{-7}$	$1.4E^{-7}$	$9.8E^{-11}$	$1.68E^{-8}$	-	0.0010457

Canned foods are very popular and extensively consumed in various regions of the world due to their low cost and affordability. The purpose of the packing process is to maximize the shelf life of food. However, due to the rapid growth of this industry, there has been a significant increase in fraudulent practices [9]. Suaad et al. [10] reported that despite the legislation set by the WHO / FAO / CAC committee, which mandates that the raw materials used in this industry must be of high quality and free from defects, numerous canned foods are being sold in local markets without undergoing quality control. Consequently, a significant number of these canned foods fail to meet the legal and health standards. These foods indirectly impact consumers' health by the deposition of certain components. The metal content in canned food is affected by several factors, including the pH of the canned product, the concentration of oxygen in the headspace, the quality of lacquer coatings on the cans, the quality of the coating, and the storage location [23, 24].

The metal accumulation varies greatly between the contents of the can. This study assessed the elemental compositions of Canned fish (Sardine) and Soyabeans and the results shows the presence of the following elements: Aluminum, Bismuth, Calcium, Iron, Potassium, lithium, Manganese, Sodium, Si: Silicon, Strontium, Thorium and Magnesium. The mean value of Al in canned sardine in this study (0.17±0.08 mg/l) was higher than Soyabean sample of 0.04±0.02 mg/l. The canned food samples concentrations of Al were generally below the CAC/FAO/WHO standards of 7.0 mg/l (Tables 1 and 2). The results were higher than those reported level in canned sardine consumed in India which was 3.16 mg/l [25]. They were also above the reported value of 0.98 mg/l [26] and 3.12 mg/l [27] in Turkey and Lebanon respectively. Manganese is an indispensable element for human survival. Additionally, it engages in the conversion of hydrocarbons and lipids and exerts a stimulating influence on enzymes, particularly those that aid in the assimilation of specific vitamins during metabolic processes. Additionally, it is necessary to uphold proper bone structure and assumes a crucial function in the synthesis of thyroxine, the primary hormone secreted by the thyroid gland. Nevertheless, in specific instances, it can provide a risk to human well-being. Manganese compounds that include oxygen exhibit a potent hazardous impact, which varies depending on their oxidation state. The primary symptoms of manganese toxicity include hallucinations, memory impairment, and nerve impairment [28]. The optimal daily allowance of manganese should not surpass values ranging from 3.0 to 9.0 mg/l [29]. The mean manganese level of canned sardine and soyabeans as recorded in this study was below CAC/FAO/WHO maximum permissible limits as shown in Tables 1 and

2. The findings are in concurrent with other studies [29, 28]. In humans, a deficit of zinc has been associated with decreased appetite, stunted growth, alterations in the skin, and issues with the immune system [30]. Low concentrations (0.003±0.00 mg/l) of zinc was only observed in Soyabeans sample but was not found in Sardine samples. The results were in agreement with others works. Iron is a crucial mineral that is highly prevalent among transition elements. It is widely recognized as a prominent metal in biological systems, where it plays a significant part in human physiology. Anemia, resulting from iron deficiency, diminishes both cognitive performance and physical labor ability. Excessive consumption of this substance has been linked to the occurrence of organ failure [30-33]. The average quantities of Iron in the samples were found to be below the maximum allowable limits set by CAC/FAO/WHO [34]. The mean values of calcium, Bismuth, lithium, magnesium, sodium, and silicon were below CAC/FAO/WHO maximum permissible limits as stated in Tables 1 and 2. This results are in accord with the studies of Mol, [30] and Wheal *et al.* [33]. The activity concentrations of natural radionuclides, specifically ^{232}Th, ^{90}Sr, and ^{40}K, in the canned Sardine and soyabeans samples are provided in Tables 1 and 2. The investigation found that the highest amounts were observed for the naturally occurring radionuclide ^{40}K. The Canned food samples exhibited the most activity when ^{40}K was present. Nevertheless, ^{40}K is a crucial biological component and its levels in human tissue are carefully regulated through metabolic processes [35]. The content of ^{40}K in the soybean sample was higher than the concentration of ^{40}K in the sardine sample in this study [35-38]. The order of the elements concentration in soyabeans sample in the study were K>Ca>Fe>Mg>Na>Si>Li>Th>Al>Mn>Sr >Bi>Zn while for canned sardine sample was K>Ca>Fe>Mg>Na>Si>Al>Th>Li>Bi>Mn >Sr. The results obtained were consistent with the research conducted by Hernandez et al. [35] and Scheibel and Appoloni [38].

4. Conclusion

The samples obtained and analyzed all indicated the presence of varying types of elements. In all, thirteen elements were detected in the two canned food (Soyabeans and Sardine) samples (Al, Bi, Ca, Fe, K, Li, Mg, Mn, Na, Si, Sr, Th, and Zn). The order of the elements concentration in soyabeans sample in the study were K>Ca>Fe>Mg>Na>Si>Li>Th>Al>Mn>Sr >Bi>Zn while for canned sardine sample was K>Ca>Fe>Mg>Na>Si>Al>Th>Li>Bi>Mn >Sr. The concentration levels of each element identified were exceedingly minute and significantly below the utmost limits established by the Food and Agriculture Organization, Codex Alimentarius Commission, and World Health Organization. Human health risk associated with ingesting the analyzed soyabeans and sardine samples was also assessed by calculating non-carcinogenic risks [estimated daily intake (EDI), Target hazard quotients (THQ), Hazard Index (HI)]. The results indicate that the non-carcinogenic risks were below allowable limits and were less than 1. This implies that their level of safety to humans is high and may not constitute a threat to human health. However, it is important to continuously monitor these products and their consumption since they are widely consumed.

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