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Tin and Aluminium Concentration in Canned Foods, Drinks and Beverages Sold in Nigerian Markets

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ABSTRACT

Concentration of tin and aluminium in twenty-four samples of different brands of canned foods, drinks and beverages sold in the Nigerian markets was determined using Graphite Furnace Atomic Absorption Spectrophotometer. This was with the aim of establishing the extent to which the containers leach into their contents and also the degree of health hazard such containers could cause. From the results obtained, for canned soft drinks; the mean average concentration ranged from <0.01-74.9µg $ml^{-1}$and for canned energy drinks and alcoholic drinks, they were below detection limits for tin but for aluminium, the mean average concentration ranged from <0.01-71.2 µg ml^{-1}. For canned beverage drinks; the mean average concentration ranged from <0.01-516.0µg ml^{-1} for tin and 9.76-387.5µgml^{-1} for aluminium and for canned foods, the mean average concentration ranged from <0.01-202.9 µg ml^{-1} for tin and 5.25-63.6µg$ml^{-1}$for aluminium . In all the analyzed samples, some products had in excess of the limits while some were below the maximum limits established by WHO/FAO and EU which says according to EC 1881/2006 maximum limit for tin which says 200mg/kg in canned food other than beverages should be 100mg/kg including fruit and vegetable juices and 50mg/kg for baby food. It could be inferred that the metals container leached into the product more at low pH than at higher pH and it can also be leached into the products as a result of poor manufacturing processes.

KEYWORDS: Concentration of tin and aluminium in the canned products, leaching, sources, toxicity.

1.0 Introduction

Heavy metals occur in all foods as natural or inherent component of plant and animal tissues and fluid and also may be present as a result of contamination or deliberate addition (Underwood, E.J., 1973). The ingestion of accumulated trace metals from canned food by man poses health hazard such as skin irritation, damage to the liver, kidney, circulatory and nerve tissues, resulting from acute or chronic exposure (Adekunle et al. 2003). The neurological aspects of poisoning from many metals indicate the nervous system as target organ with respect to metal toxicity. Other target organs are gastrointestinal tract, respiratory tract, blood, and kidney, bone, nails, hair, endocrine (ASTDR., 1993). When the concentrations of the metals are beyond the tolerable limit, they become toxic.

1.1 The toxicity and dissolution of tin and aluminium

Tin exists in two oxidation states, as divalent tin Sn^{2+}, tin (II) and as tetravalent tin (IV). Dissolution of metallic tin from a can body into the food contents will result in it, being present in the divalent form. One of the factors affecting its presence is pH. At pH>2, tin forms $Sn(OH)_2$ which has low solubility . Other chemicals which may also be present in food stuffs and known to complex with tin are alcohols and high fatty acid, citric, tartaric and oxalic acids (Steve, B et al. 2003) .Reactions involving the reducing properties of tin can also occur. Therefore, the bioavailability of potentially toxic tin in food depends on the quantity of food ingested and pH, oxidation state, extent of complexation or adsorption, and solubility. Tin is not absorbed after ingestion and its toxic responses may be due to gastrointestinal irritation and not systemic poisoning (Steve, B et al. 2003).Storage conditions such as temperature, affect the rate of dissolution of tin into canned food. After detinning, delaminating and leaching of alloying metals into the contents will then results (A.U. Itodo et al.2009). Studies of the increasing concentration of tin in food with respect to the time after filling the can have been made in canned vegetables (Arvanitoyannis, I., 1990b). It was reported that concentrations of total tin in conserves of acidic fruit, such as fruit juice. The combustion of fossil fuels contributes to the amount of tin in air. Excluding point source industrial emissions, tin levels in air have been found to be generally less than 0.3µg/cm^3 and the intake of this metal from air would therefore be less than 6g/person/day (MAFF., 1985) in most unprocessed food, tin are generally less than 1µg/g.

2.0 Legislative controls of metals in canned food, drinks and beverages and literature review

According to EC 1881/2006 maximum limit for tin (in mg/kg wet weight) are: (i) 200 in canned foods other than beverages (ii) 100 in canned beverages including fruit and vegetable juices and (iii) 50 in baby food (JECFA., 2001).The Provisional Tolerable Weekly Intake for tin is 14 mg/kg body weight, equivalent to 120mg/day for an adult (MAFF., 1993) and recommended maximum permissible levels of tin in food are typically 250 mg/kg (200 mg/kg) (Codex., 1998) for solid foods and 150 mg/kg for beverages (EFSA., 2008). Higher concentrations of tin are typically found in canned foodstuffs as a result of dissolution of the tin coating or tin plate, the levels depending largely on the type and acidity of the food, the presence of oxidants, the duration and temperature of storage and the presence of air in the can headspace (Blunden et al., 2003).

(Omori, Y., 1996) reported that a canned orange-based drink containing 425ppm tin produced a similar outbreak of intoxications, manifested by nausea, Vomiting, diarrhea, fever and headache. (Svensson, V., 1975) reported a study showed that 99.5% of 1200 tested cans contained below the UK regulatory limit of 200mg/kg of tin, an improvement over most previous studies largely attributed to the increase due to fully lacquered cans for acidic foods, and concluded that the results do not raise any long term food safety concerns for customers.
The world health organization (WHO) reported in 1989 that the Provisional Tolerance Weekly Intake (PTW I) is 7 mg of aluminum /kg body weight. The acceptable dosage is therefore not more than 60 mg/ day for a person weighing 60 kg (FAO, 1986). Recently at its sixty-seventh meeting, JECFA re-evaluated aluminium from all sources, including food additives, and established a PTWI of 1mg/kg bw which is seven times lower than the previous PTWI. JECFA also noted that the PTWI is likely to be exceeded to a large extent by some population groups, particularly children, who regularly consume foods that include aluminium-containing additives.

3.0 Materials and methods

3.1 Materials and Reagents

Appropriate quality assurance procedures and precautions were carried out to ensure reliability of the results. To eliminate possible contamination from detergents or other sources, all glass wares and polyethylene material used was were soaked with a 1M nitric acid for 48h and then rinsed several times with distilled water before use. Concentrated hydrochloric acid and Nitric acid used, were of analar grade (Sigma, St. Louis, MO, USA). Distilled water used was produced from the physical Chemistry laboratory of the Department of Pure and Industrial chemistry, University of Nigeria, Nsukka which was used for all washings and dilutions.

3.2 Apparatus

Oven -Memmert D-91126 (Schwabach, Germany), Weighing balance (E. mettler Zurich analytical balance, Switzerland), P^H meter (JENWAY MAKE MODEL 3510), Matrix modifier, Graphite furnace atomic absorption spectrometer Accusys 211 (Atomic Absorption spectrophotometer model 220-GF) and Filter paper (Whatman filter paper No.4).

3.3 Sample Collection

A total of twenty-four (24) samples of canned foods and drinks investigated were purchased from super market and local retail outlets in Nsukka Community, Enugu state, Nigeria. The samples chosen were considered to be a fair representation of the canned drinks, foods and beverages available on the Nigerian markets.

3.4 Sample preparation for canned drinks and beverages for tin

Canned drinks and beverages were degassed before analysis, 15cm^3 of canned drink was pipette and 15 cm^3 of concentrated HCl and 15 cm^3 of concentrated HNO_3 were pipette into the canned drink heated on a hot plate under fume cupboard to severe boiling, the solution were fully digested and reduced to 10 cm^3, the solution was allowed to cool and then filtered into 100 cm^3 volumetric flask and made up to mark with distilled water and empty into container for further treatment.

3.5 Sample preparation for canned drinks and beverages for aluminium

Canned drinks and beverages were degassed before analysis, 15 cm^3 of canned drink was pipette and 15 cm^3 HNO_3 acid was pipette into the canned drink heated on a hot plate under fume cupboard to boiling until the solution were fully digested and reduced to 10 cm^3, warm distilled water was added to it. The solution was allowed to cool and then filtered into 100 cm^3 standard flask and made up to mark with distilled water and empty into container for further treatment.

3.6 Sample preparation for canned foods

After opening, each can content was homogenized thoroughly in a food blender with stainless steel cutters then some quantity of about 30g of each sample was transferred into a stainless steel pan and they were all transferred into an oven and baked at 100°C for between 60-180 minutes kept in an oven at 60°C for 72h until dried, and grounded into homogenized fine powder.

1g each of homogenized sample were weighed and completely transformed into different 100 cm^3 beaker each, 15 cm^3 of Conc.HNO_3 were added and was heated in a fume cupboard to boiling until the solution were fully digested and reduced to 10 cm^3 then 15 cm^3 of Conc.HCI was added and heated gently until the sample bumping (from evolution of Cl_2) stopped, warm distilled water was added to it then the solution was allowed to cool and filtered into a 100 cm^3 volumetric flask and made up to the mark with distilled water.

3.7 Sample analysis

Aluminium and Tin determination by GF-AAS

0.25 cm^3 matrix modifier concentration in µg/ml ± 5.0g (2.0g palladium in 2g HNO_3) was added to all samples to normalize the desired element into a form that is not easily volatilizing from halogen in the ashing step into a suitable atomic absorption. The sample and the mixture was mixed together and filtered with filter paper.
2 cm^3 of the blank and the standards for each metal (Al) were poured into auto-sampler cup and 20µL of high standard was first injected and aspirated into the furnace.

In the auto-peak timing mode, the software determined the best integration window for the peak and then continues with the blank and other standards to calibrate the instrument and generate the calibration curve.
2 cm^3 each of the sample filtered was poured into auto-sampler cup numbered S1-S11 for each metal (Al), then 20µL of each sample was injected and aspirate by pressing READ/START button to run the sample with the appropriate lamp for the element of interest.

pH meter determination

pH was determined using digital pH Meter (JENWAY MAKE MODEL 3510) at room temperature of 28.2°C and 28.1°C respectively for each of the samples. 10ml of sample was taken into beaker and pH electrode was dipped inside it and the solvent used was distilled water and pH meter was standardized before any determination was taken.

4.0 Results and discussion

The operational settings and analytical conditions of the instrument for the determinations are presented in Table 1.These conditions ensured accurate determinations.

Table1: Operational settings and the analytical conditions of GF-AAS for tin and aluminium determinations.

Operational Settings	Analytical Conditions
Lamp current low (mA)	10
Lamp current high (mA)	600
Wavelength for tin	286.3 nm
Wavelength for aluminium	309.3 nm
Slit width	0.7 nm
Lamp mode	BGC-SR
Sample volume	20 µL
Concentration unit	PPb
Repetition Sequence	S1-S11
Fuel gas flow rate	7.0 $Lmin^{-1}$
Zero intercept	Yes
Background gain	1

Table 2: Mean concentration of tin, aluminium and pH of canned alcoholic drink.

MEAN CONCENTRATION VALUES, µg ml^{-1}			
SAMPLES	**CONCENTRATIONS AND STANDARD DEVIATION FOR Sn**	**CONCENTRATIONS AND STANDARD DEVIATION FOR Al**	**pH**
Canned Star	<0.01 ± 0.89	5.25 ± 2.98	5.59(acidic)
Heineken	<0.01 ± 0.22	11.61 ± 3.67	5.65(acidic)
Trautwein Red wine	<0.01 ± 0.57	5.51 ± 2.06	6.66(acidic)
Smirnoff(Ice)	<0.01± 5.6	63.6 ± 90.4	4.99(acidic)

In this table 2, all the analyzed samples for tin and aluminium concentration comprising of canned star, Heineken, trautwein red wine and smirnoff ice drinks were observed to be < 0.01µg ml^{-1} with different in their pH values meaning they were below detection limits while that of aluminium ranged from 5.25-63.6 µg $ml^{-1}$and they have not in any way violated the rules sets by WHO/FAO (1997), EU (2008), JECFA (2001) guidelines. Correlation of the tin, aluminium and pH value of the samples, it showed that there is no direct correlation between the degree of acidity and the metal content. However, there is need for investigations to find out if the alcoholic nature of the products has any effect on the degree of the leaching.

Table 3: Mean concentration of tin, aluminium and pH of canned beverage drinks.

MEAN CONCENTRATION VALUES, µg ml^{-1}			
SAMPLES	**CONCENTRATIONS AND STANDARD DEVIATION FOR Sn**	**CONCENTRATIONS AND STANDARD DEVIATION FOR Al**	**pH**
Canned milo	< 0.01 ± 0.99	14.45 ± 8.89	8.16(alkaline)
Peak milk	< 0.01 ± 0.24	9.76 ± 2.94	7.81(neutral)
Olympic milk	217.6 ± 45.4	228.3 ± 337.4	7.51(neutral)
Three Crown milk	516.0 ± 119.7	387.5 ± 599.2	7.62(neutral)
Five alive juice drink	<0.01 ± 0.42	37.3 ± 80.2	5.41(acidic)

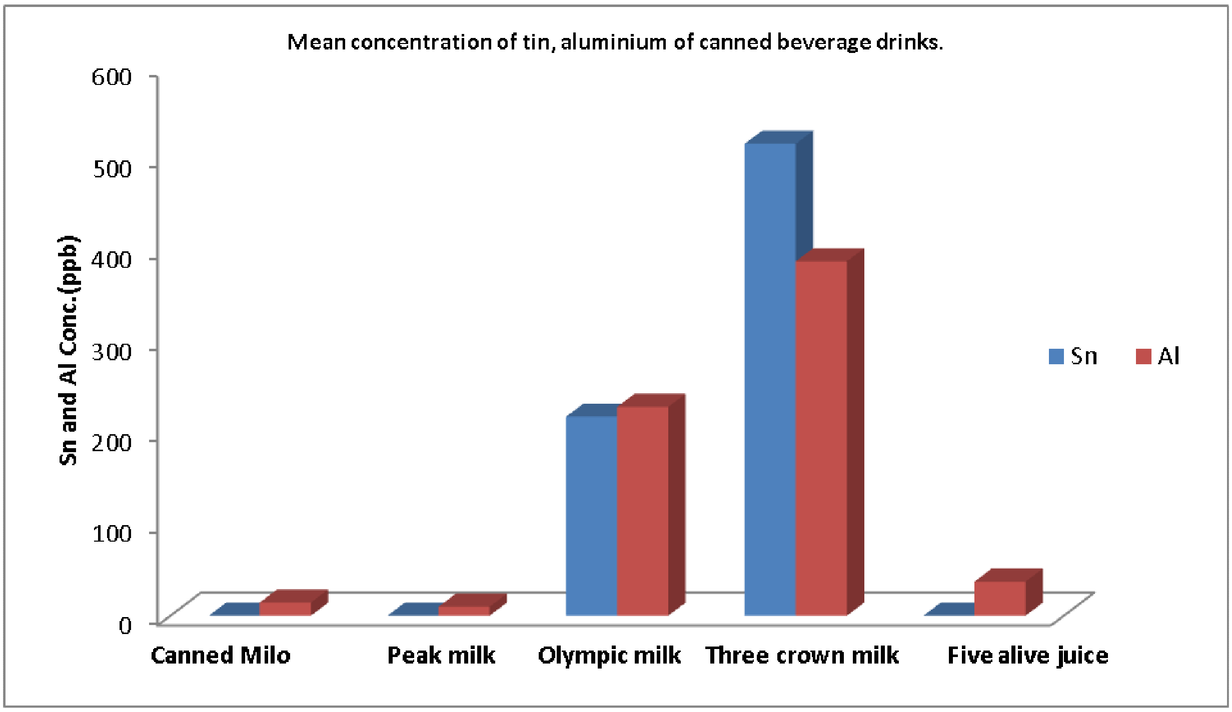

Fig.1: **Mean concentration of tin and aluminium in canned beverage drinks**

Table 3 and Fig.1 are display of tin and aluminium concentration of the canned beverage drinks. This tin and aluminium are compared with pH values of the beverage drinks. From the results obtained, it could be seen that tin value ranges from <0.01-516.0μgml^{-1} while that of aluminium ranged from 9.76-387.5 μgml^{-1} . The highest mean concentration of these two metals were found in Three crown milk and olympic milk respectively. Three crown milk has the highest value of 516.0±119.7μgml^{-1}for tin and 387.5 ± 599.2 μgml^{-1}for aluminium with a pH value of 7.62 followed by Olympic milk with tin value of 217.6±45.4μg ml^{-1} and 228.3± 337.4 μgml^{-1} for aluminium with a pH value of 7.51while canned milo has the lowest value of <0.01±0.99μgml^{-1}and with a pH value of 8.16 and Peak milk has the lowest value of <0.01±0.28μgml^{-1} for tin only and 9.76±2.96 μgml^{-1} for aluminium with a pH value of 7.81.The tin and aluminium concentration when compared to WHO/FAO (1997), EU (2008), JECFA (2001) guidelines, indicates that Three crown milk and Olympic milk has violated the imposed rules while canned Milo and peak milk were below the safety limits. Correlation of the tin and aluminium contents and pH value of the samples show that there is no direct correlation between the degree of acidity and metal content. It is obvious that some metal dissolve into the food content, particularly when uncoated internal surfaces are used. These findings are consistent with studies from other researchers which support the conclusion that canned drinks are not free of contamination during processing and even with heavy metal content (Blunden et al., 2003).

Table 4: Mean concentration of tin and pH of canned foods.

SAMPLES	CONCENTRATIONS AND STANDARD DEVIATION OF Sn	pH
Canned meat	202.9 ± 232.9	4.3(acidic)
Gino tomatoes	<0.01 ± 0.02	3.8(acidic)
Canned maize	13.4 ± 57.1	5.7(acidic)
Titus	<0.01 ± 0.64	6.5(acidic)

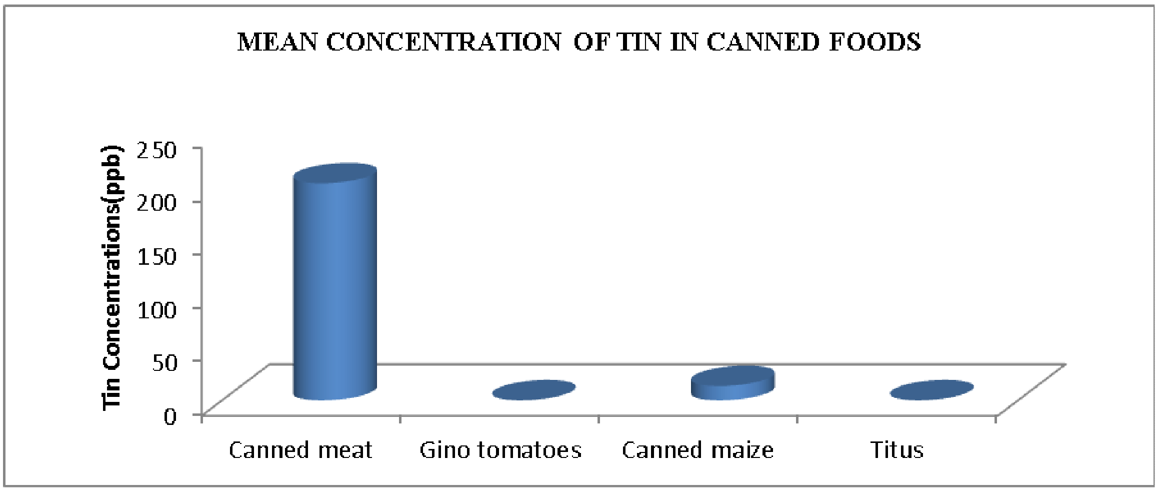

Fig.2: **Mean concentration of tin in canned foods**

Table 4 and Fig. 2, these are display of tin concentration of the canned foods. This tin value is compared with the pH values of the samples. From the results obtained, it showed that the tin value ranges from <0.01-202.9µg ml^{-1}.Canned meat has the highest mean concentration of 202.9±232.9µgml^{-1} and with a pH value of 4.3 followed by canned maize which has concentration of 13.4±57.1µg ml^{-1} and with a pH value of 5.7 while Gino tomatoes has a concentration average of <0.01±0.02 µg ml^{-1} and with a pH value of 3.8 and Titus has tin value of <0.01±0.64 µg ml^{-1} and with a pH value of 6.5 which were the lowest concentrations. Compared the results obtained with the EU (2008) guidelines, it can be said that canned meat was above the imposed limits while canned maize, Gino tomatoes and Titus were below the safety limits. Correlation of the tin and pH value of the samples, it showed that there is a direct correlation between the degree of acidity and metal content, implying that at lower pH more of the metal container leached into the drinks than at higher pH. However, there is need for investigations to find out if canned meat has any effect on the degree of the leaching into the product.

Table 5: Mean concentration of tin and pH of canned soft drinks.

SAMPLES	CONCENTRATIONS AND STANDARD DEVIATION OF Sn	pH
Canned maltina	< 0.01± 1.04	6.43(acidic)
Canned fanta	0.31± 3.13	4.21(acidic)
Chivita pineapple	< 0.01± 0.74	5.16(acidic)
Lucozade boost	<0.01± 0.14	4.64(acidic)

Table 5 shows that tin concentration of canned soft drinks ranged from <0.01-0.31µg ml^{-1}. From the figure, it could be seen that canned Fanta has the highest concentration of 0.31±3.13µg ml^{-1} and with a pH value of 4.21 while other which includes canned Maltina, Chivita fruit juice and Lucozade boost have the lowest tin value of <0.01µg ml^{-1} meaning they were below detection limits. Comparing tin concentrations to the EU (2008), WHO (1997) and JECFA (2001) guidelines, it was observed that they were below the safety limits. Correlation of the tin content and pH values shows that there is no direct correlation between the degree of acidity and metal content. Influence of pH on metal level is not clearly seen from the results obtained. This implies that low pH may or may not have aided the leaching of the metal container into the foods and drinks, this could be depended on the type of aluminium containers used. The lower concentration of aluminium in canned soft drinks is already well documented and the present results are in good agreement with the literature data of EU (2008), WHO (1997) and JECFA (2001) guidelines.

Table 6: MEAN CONCENTRATION OF ALUMINIUM AND pH OF CANNED SOFT DRINKS

SAMPLES	CONCENTRATIONS AND STANDARD DEVIATION OF Al	pH
Capri-sonne fruit	74.9 ± 8.0	4.93
Canned Fayrouz	6.7 ±32.8	3.44
Canned Sevenup	<0.01 ±10.2	4.51
Canned maltina	12.23 ± 0.02	6.43
Dansa fruit juice	<0.01 ±13.2	4.56
Canned fanta	12.86 ±5.95	4.21
Chivita fruit juice	9.99 ± 2.77	5.16

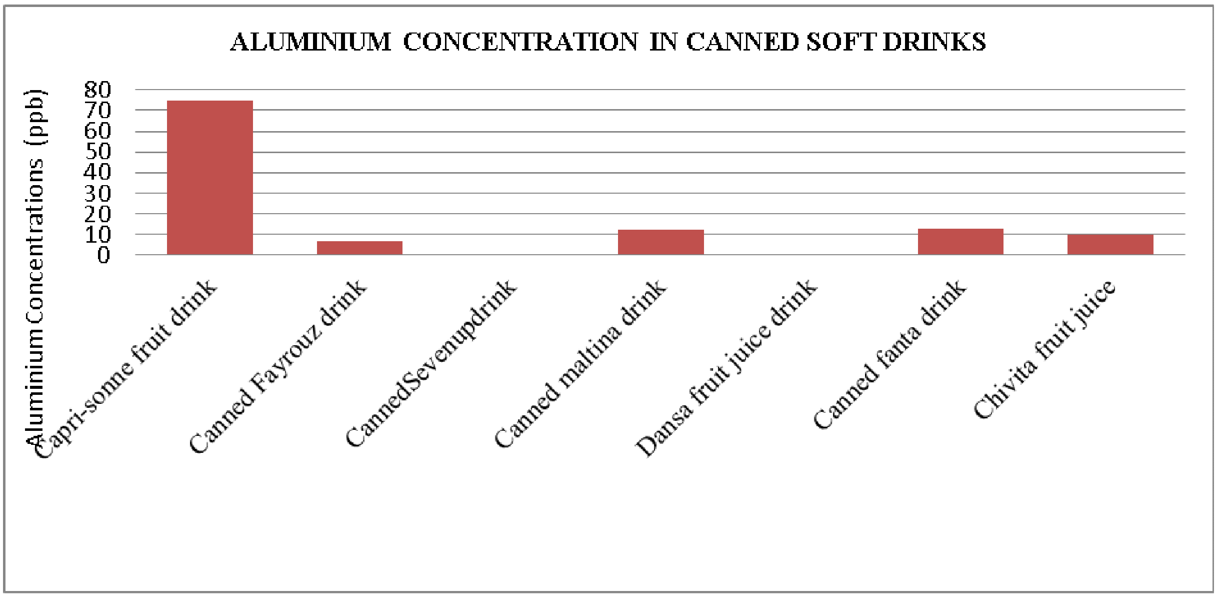

Fig.3:Aluminium concentration in canned soft drinks

Table 6 and Fig. 3 shows the aluminium concentration of canned soft drinks which ranges from <0.01-74.9µgml^{-1}. The Al value is compared with the pH value of the samples. From the results obtained, it could be seen that Capri-sonne drink has the highest aluminium value of 74.9 ± 8.0µgml^{-1} and with a pH value of 4.51 followed by canned Fanta with concentration average of 12.86 ± 5.95µgml^{-1} and with a pH value of 4.21. Seven-up drink and Dansa fruit juice has the lowest aluminium concentration that is seven up having <0.01±10.2µgml^{-1} and with a pH value of 4.51 and Dansa fruit juice having concentration average of <0.01±13.2µgml^{-1} and with a pH value of 4.56.The Al concentration when compared to EU guidelines, the analyzed samples were below the imposed limits.Correlation of the aluminium content and pH value of the samples shows that there is a direct correlation between the degree of acidity and the metal content, implying that at low pH more of the metal container leached into the drinks than at higher pH. These findings are contrary to earlier findings which say that canned drinks are not free of contamination during process and even with heavy metal content (Blunden et al.,2003).

CONCLUSION

The obtained method validation demonstrated that the studied method corresponds for the Sn and Al concentrations determination in different canned foods and drinks using GF-AAS, the method being efficiently and properly implemented. It was observed that some products had in excess of the limits while some were below the maximum limits established by WHO/FAO, JECFA, and EU. However, amount of metal ingested will depend on the quantity and frequency of food consumption.

EVALUATION

This research work has confirmed the presence of tin and aluminium in most of the canned foods, drinks and beverages sold in Nigerian markets. It was discovered that the amount of tin and aluminium found in some products do not appear to pose any acute toxicological problems in the human system whereas some do pose serious toxicological problems. From the results obtained, it is imperative for the safety organizations in our country to make sure that all the manufacturing industries abides by the rules and regulations set by WHO/FAO etc.

RECOMMENDATIONS

The WHO, EU, FAO and JECFA Committees recommends that efforts should be made to keep tin and aluminium levels in canned foods, drinks and beverages as low as practicable. In this regard, tin and aluminium concentration in canned foods and drinks have to be restricted to those coherent with the application of good manufacturing practices [15]. However, the amount of metal ingested will depend on the quantity and frequency of the canned foods, beverages and drinks consumption. Further studies should be carried out to find out if the duration of storage i.e. storing the products for a period of three to four years in a particular room and also to check if the additives which are usually added to canned products for preservation could be a contributing factor to the leaching of the metal into the product.

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