ESTIMATION OF TOXIC METALS IN CANNED MILK PRODUCTS FROM UNLAQUERED TIN PLATE CANS.

[1] Itodo U. Adams and [2] Itodo U. Happiness

[1]Department of Applied Chemistry, Kebbi State University of Science and Technology, Aliero, Nigeria.
[2]Department of Chemistry, Benue State University, Makurdi,Nigeria
itodoson2002@yahoo.com

Abstract: Branded canned milk (B1, B2, B3 and B4) were selected in triplicate, using market basket approach. The samples were pre-treated and analysed for heavy metals. Their physicochemical variables were estimated. The metal concentration (in μgg^{-1},using AAS)of some toxic metals compared to those of uncanned dairy products include: 0.02±0.008 (006±0.003); 1.61±0.21 (0.01±0.01); 1.47±0.73 (0.01±0.01); 1.64±0.66 (0.05±0.03) and 1.75±0.29(1.54±1.2) for Cd, Co, Cr, Ni, and Pb found in canned and (uncanned) milk products respectively. Further analysis revealed that Nickel contents in milk is less, compared to those of canned fish products. Unlike Cd contents, Cr and Pb concentration were above the threshold limit values (TLV) of $2.0\mu gg^{-1}$. . [Journal of American Science 2010;6(5):173-178]. (ISSN: 1545-1003).

Key words: Toxic metals, canned milk, Corrosion, Health

1. Introduction.

Research achievements that contribute to prevention of disease are not as dramatic as the discovery or implementation of cures for existent disease but are certainly no less important. Research regarding the health effects of toxic metals may make a small contribution that helps millions of people, but is probably unknown to them. While these epi-beneficial effects may not be apparent to the individuals who are spared the problems of toxicity, the implementation of measures to reduce exposure to these toxins are clearly visible when examined on a population basis (Robert,1996). It is necessary to keep food preserved for a considerable period such that when required, it will be in a state, fit for consumption. That is, the food is kept free of mould and bacteria growth. Food canning implies the storing of food in airtight containers. The food is preheated to bring about the destruction of organisms (Kenneth and Helen; 1947). The lethal effect of heat on micro organism has been used for food preservation long before the microbial causes of food spoilage was discovered. Pasteur showed that the spoilage of milk could be prevented by holding the milk for a few minutes at a temperature between 50-70^0C (Ngoddy and Ihekomonye, 1992). Canning of food product is the sealing of the food products after heat treatment (Itodo *et al.,* 2009).

Tin plate is light gauge, steel sheet or strip coated on both sides with pure tin. (Steve *et al.,* 2003). They are important containers for packaging of food, including milk and for heat

processing. The properties of open tin plates which make it an ideal canning material are; Strength and rigidity, Ability to be worked at high speed for the construction of can bodies and ends, formation of a double side seams, good corrosion resistance under normal storage condition, attractive appearance, ability to withstand high pressure and high processing temperature and ease of shaping and decorations. Tin plate cans usually consist of central core of base steel covered on each surface by a layer of oxide and finally a thin film of oil. Lacquered tin plate (tin plate with synthetic substance that form a hard protective coating) has another layer, usually on one side (Ngoddy and Ihekomonye, 1992).When the Tin plate cans are not lacquered, alloying metals which make up the electrolytic composition of the cans may easily leach out of corroded cans.

Mechanism of Metal Toxicity: Metallic toxicant in canned milk, through exposure or ingestion may find their way into the body, at such, may act through one or more of these possible mechanisms

(a) **Inhibition of Enzymatic Activities**: This is so because some metals such as Pb, Hg and Cd have affinity for sulphur and therefore attack sulphur bonds in enzyme, thus immobilizing them. Other site of attack include the free amino ($-NH_2$) and carboxyl (-COOH) groups in protein (Ademoroti, 1996 ; Alka, 2000).

(b) **Attacks on Cell Membrane and Receptor**: The heavy metals bind to cell membrane and receptor, thereby altering their structures. This affect transport and other inter or intra cellular processes in the body. Cd inhibits oxidative phosphorylation in the body (Alka, 2000).

(c) **Interference with Metabolic Cations**: Heavy metals interfere with the metabolism of essential cations such as absorption, transportation, decomposition and storage. Cd follows the pathway of Zn and Cu metabolisms. Pb replaces Ca in bones (Michael and Peter, 1990). This is the most crucial aspect of metals that leads to manifestation of toxic effect.

(d) **Action on the Artery**: Heavy metals can increase the acidity of the blood. The body draws Ca from the bones to help restore blood pH. Further toxic metals set up conditions that lead to inflammation in arteries and tissues, causing more Ca to be drawn to the area as a buffer. The Ca, coats the inflamed area in the blood vessel but creating another by the hardening of the artery walls and its progressive blockage of the arteries. This leads to osteoporosis (Michael and Peter, 2003)

Heavy metals in canned food had its source traced to the untreated water, chemical residue in processed foods, leachates, bio – accumulation in aquatic animals and industrial emission into food before packaging or canning (Goyer, 1991).

pH and Leachates Concentration: Most proteins exhibit maximum stability in cans but not at the pH in which they naturally occur. Most protein are denatured at pH < 3 or > 10. At this stage, the leachate is either enriched with heavy metals within the food material or cans depending on the pH of the medium. Direct uptake of heavy metal by the food material before canning, as a result of processing or as a result of storage and distribution. In other words, leachate enrichment with heavy metals can be from the food or from the containers all depending on pH and other denaturing agents.

Chemistry Involved In Leaching of Metals from Cans: The chemistry involved in heavy metal delamination into canned food involves the following step: Detinning/corrosion, rusting of cans and leaching of the toxic metal from the corroded cans. Detinning is the removal of the tin coating. It occurs at pH > 2, rendering the inner container unprotected. This process is due to the action of oxygen

$$1/_2O_{2(g)} + H_2O_{(g)} + 2e^- \longrightarrow 2OH^-$$

$$NO^-_{3(aq)} \longrightarrow NO_{2(g)} + O_{2(g)}$$

$$Sn \longrightarrow Sn^{2+} + 2e$$

$$Sn^{2+} + 2OH^- \longrightarrow Sn(OH)_2$$

The Sn $(OH)_2$ has low solubility and can cause gastro-intestinal disorders,

Rusting of the tinplate cans begins during and after the detinning following the reaction below:

$$Fe_{(s)} \xrightarrow[\text{(oxidation)}]{} Fe^{2+}_{(aq)} + 2e^-$$

$$2H^+ + 2e^- \xrightarrow[\text{(reduction)}]{} H_2$$

$$Fe + 2H^+ \longrightarrow Fe^{2+} + H_2$$

$$Fe^{2+} + 2H_20 \longrightarrow Fe(OH)_2 + 2H^+$$

$$Fe_{(s)} + 2H^+ \xrightarrow[{[O]}]{} Fe^{2+} + H_2O \longrightarrow Fe(OH)_2$$

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

$$Fe(OH)_2 \xrightarrow[\text{(corrosion)}]{} Fe_2O_3\ .xH_20$$

Brown hydrated iron (iii) oxide.

The above reactions render the can plate, porous thereby effecting the ease of leaching of alloying metals (Charles, 1999; Ngoddy and Ihekomonye, 1992; Steve and Wallace, 2003). This present work was embarked upon to estimate the heavy metal contents of various canned milk from village markets in Sokoto state, Nigeria, for the purpose of providing data for future compilation of Nigerian food consumption table, display of health implications for the populace and for use by the Nigerian Standard Organizations.

2. Materials and Methods

Triplicates of four brands of canned milk stored in Unlacquered cans were randomly bought from village markets in Sokoto state, Nigeria. Two analytical techniques were employed viz: the flame photometer, used for preliminary analysis followed by the Atomic Absorption spectrophotometer.

Sample Preparation for Protein Determination (Kjeldahl Method): 2.00g each of the blended material was placed into a Kjeldahl flask and 20cm^3 of water was added. The flask was shaken for two minutes and was allowed to stand. One tablet of mercury catalyst or Kjeldahl digestion tablet was added followed by 30cm^3 of concentrated H_2SO_4. The contents in the digestion tubes were heated continuously at 100^{0}C in the digestion block. When water was removed and frothing ceases, the heating was continued for two hours for complete digestion indicated by the disappearance of original canned food to give a clear solution. This is followed by cooling of the samples and dilution to 50cm^3 with water (AOAC, 1990).

(b) Procedure for Protein Analysis

20 cm^3 of the digest was pipetted into another microKjeldarhl digestion and distillation apparatus. 25 cm^3 of boric acid indicator was added in the

conical flask placed under the condenser of the apparatus. 20 cm^3 of 10M NaOH was added to the content of the flask by opening the cock through the distillation flask. The heat supplied was regulated to avoid sucking back. The condenser was kept cooled by passing cold water. When all the available distillate has been collected in 25 cm^3. of boric acid, the distillation was stopped and set for further analysis. The nitrogen in the distillate was determined by titrating with either 0.01M or 0.1M HCl. The colour change at end point was from green to blue (Ceirwn, 1995).

Physicochemical Variables

(a) Determination of Moisture Content

5g each of the blended food sample was weighed in a previously weighed porcelain dish. The samples was dried in the Galenkamp side two oven operated at 105^0C, for three hours, cooled in a dessicator containing silica gel overnight before re-weighing (AOAC, 1990)

(b) Determination of Ash Contents

The dried sample was used for ash determination. The sample in the porcelain dish was fed into the furnace at a temperature of 700^OC and was allowed to normalize. Ashing was done for four hours after which the sample was removed and placed in a dessicator containing silica gel. Alternatively, the fresh sample is left overnight in the furnace and later weighed. The percentage ash was calculated. Wet digestion, including the Nitric Acid – Hydrogen Peroxide (HNO_3/H_2O_2) and Nitric Acid – Sulfuric Acid (HNO_3-H_2SO_4) methods (earlier described by AOAC, 1990; Itodo *et al*., 2009 and Ademoroti, 1996) was adopted to leach the metals into the analytical solutions.5 cm^3 of water was added to the digest and was allowed to cool, followed by filtration using the Whatman filter paper No.42. The solution was neutralised with conc. NH_4OH, transferred into a 25ml volumetric flask and diluted to the mark (Ademoroti 1996).The Unicam 969 AAS was set up according to manufacturer's instruction with the wavelength corresponding to that of the element under investigation. The spectrometer was set to zero absorbance using the blank solution. The absorbance of each sample was read with an automatic calculation of the average (μgg^{-1}) .The machine (Windaus L.F. 2400 photometer) was also set up according to manufacturer's instruction with the wavelength corresponding to that of the element under analysis. The photometer was set to zero using the 0 mg /cm^3 solution. The absorbance of each sample in the sample cell was measured in duplicate.

3. Results and discussion.

The sampling data (Table1) and results of the physicochemical variables (Table 2) were presented below. The entire brands are legislatively accepted into markets, thus, tagged with the NAFDAC numbers. In their Market Basket Surveys ,Nigerian Food and Drug Administration and Control(NAFDAC), indicate federal law which provides a Medicaid benefit package for the populace through the Early and Periodic awareness campaign, Screening, Diagnosis and Treatment for toxic metal poisonings, including chelation therapy, vitamin and mineral supplementation, medical care, environmental investigations, education services, and nutritional developmental assessments.

Table 1: Sampling and Nutritional Data of Various Canned Food as at November, 2005.

Canned milk products	Net wt.	Man. Date	Exp. date	Shelf life (months)	Food duration in cans	Ingredients
B1	170g	Oct, 2004	Oct 2005	12	1 month	Milk fat, cow milk, Veg. oil, Vit A, D3 and E and 28 other vitamins
B2	170g	Oct. 2004	Oct. 2005	12	1 month	Skimmed cow milk, veg. oil, vit. A,D3 and E
B3	170g	Aug. 2003	Aug. 2005	24	15 months	Full cream cow milk, H_20, Vit A and D3
B4	170g	Oct. 2003	Oct, 2005	24	13 months	Cow milk, Vit D2 and stabilizer

Two important parameters that enrich leachates metal concentration were measured (Table 2). Mean value of 16.69±1.25% and 69.50±1.91% were reported for the protein and moisture contents respectively. Most

proteins exhibit maximum stability in cans but not at the pH in which they naturally occur. protein are denatured at pH < 3 or > 10. At this stage, the leachates are either enriched with heavy metals within the food material or cans depending on the pH of the medium. Many protein foods precipitate at their isoelectric point. (Ngoddy and Ihekomonye, 1992; Cesar *et al.*, 2001; Danute,2001).

Table 2: pH, Conductivity, Protein, Moisture, Ash and Organic Matter Content of Canned Milk Products

	Metal Concentration (µgg^{-1}),using															
		(i)AAS							(ii) Photometric analysis.							
Canned Milk	Cr (i)	Pb (i)	Cd (i)	Fe (i)	Ni (i)	Co (i)	Zn (i)	Mg (i)	Cr ii)	Pb (ii)	Cd (ii)	Fe (ii)	Ni (ii)	Cu (ii)	Al (ii)	Mn (ii)
B1	1.68	0.01	0.01	0.95	2.03	2.00	1.80	12.53	0.43	4.38	0.78	4.25	3.38	1.66	3.38	4.50
B2	0.45	0.02	0.02	1.58	1.53	1.60	1.63	19.78	0.63	4.50	0.55	3.88	3.38	1.38	3.38	4.38
B3	2.20	0.02	0.02	0.80	0.75	1.60	1.28	16.30	0.48	.13	0.71	4.38	3.30	2.04	3.30	4.25
B4	1.48	0.03	0.03	1.53	2.23	1.53	2.30	13.90	0.53	5.75	0.78	5.23	3.25	1.38	3.25	4.00
Mean	1.45	1.12	0.02	1.22	1.64	1.68	1.75	15.63	0.53	4.69	0.71	4.44	3.33	1.62	0.22	4.26
±	±	±	±	±	±	±	±	±	±	±	±	±	±	±	±	±
S.D	0.73	0.48	0.008	0.40	0.66	0.21	0.29	3.18	0.07	0.72	0.11	0.57	0.06	0.31	0.14	0.07

Table 3 presents mean value of triplicate analysis for the level of heavy metals in four brands of canned milk products. It is evidence that the levels of toxic metals falls within ranges for those reported in literature. The values of heavy metals measured in this study were compared with those in literature. The results for micronutrients like Cu, Fe, Mn and Zn indicate higher concentration for Fe and Zn than those of Cu and Al. This is in agreement with result obtained by Cesar (Cesar *et al.*, 2001).

The mean range for values of Cd contents (0.02 ± 0.008µgg^{-1} using AAS and 0.71 ± 0.11 µgg^{-1} using photometer) is low compared to that of any other metals analysed. Cadmium concentration, according to Kent ,(2003), is generally low in canned food The high Cd concentration in milk and fish product could be traced to contaminated water waste into river with subsequent flow through the food chain (Abdulrahman and Itodo, 2006).

Table 3: Toxic metal concentration of canned milk in Unlacquared tin plate cans, using (i) AAS and (ii) photometric analysis.

CANNED MILK PRODUCTS	**PHYSICOCHEMICAL VARIABLES**					
	pH	Conductivity (µs/Cm)	Protein content (%)	Moisture content (%)	Ash Content (%)	Organic solid (%)
B1	6.05	1.00	15.69	70.00	2.00	28.00
B2	6.16	1.00	17.29	72.00	2.00	26.00
B3	5.77	1.00	15.63	68.00	2.00	30.00
B4	5.52	1.00	18.18	68.00	2.00	30.00
Mean	5.87	1.00	16.69	69.50	2.00	28.50
±	±	±	±	±	±	±
S.D	0.29	0.00	1.25	1.91	0.00	1.91

The lead (Pb) content level in canned food depends on the method used to seal the cans. Contrary to this is the use of welded or lacquered cans with low lead content (Danute, 2000). Mean lead value (1.12 ± 0.48 µgg^{-1}) was obtained. A blood Pb level greater than 1.0µg/cm^{3} is dangerous to health (Adekunle, 2003).Value from the photometric analysis of Pb in milk (1.45± 0.73µgg^{-1}). This value is above recommended dose (0.10µgg^{-1}) by the existing legislation (Cesar *et al*, 2001).Food is the central source of Cu as an essential element available to man (WHO, 1996). From this study, the mean level of Cu is 1.62 ± 0.31 µgg^{-1}.

Comparative study

Two sets of comparative studies were carried out to justify the accumulation of toxic metals due to canning processes. Seven different metals estimated in canned milk (Table 4) presented values that are higher than those of their corresponding uncanned Diary products in the mean ratio of 1:3.3, 1:17, 1:14.7, 1:5, 1:32.8, 1:10 and 1:1.1 for Cd, Co, Cr, Ni, Pb, and Zn respectively. It thus follows that Nickel, a toxic metal in canned milk presented values that is 33 times higher than Ni in uncanned Diary products. It also implies that comparing Ni in canned milk to those of other canned food is critical for study.

Nickel (Ni) in canned milk and other canned products.

Nickel is trace in the environment but in higher concentration in a number of mineral ores like nickel sulphide, oxides and silicates (ATSDR, 1993). They are also found in hydrothermal veins-channels and surface deposit formed by erosion and weathering of rocks, volcanic eruption, meteorites concentrate. Trace amount of Ni are found in household products from faucet to shampoo.

Most form of Ni do not pose any threat to human health, however, large doses of it such as accidental ingestion, have been recognized with effects as stomach ache, heart failure, lung tumors, cancer, allergic skin reactions and dermatitis(ATSDR, 1993). Other research have shown that workers who inhaled Ni dust in metal processing and refining industries and workers who inhaled Ni-containing fumes from welding stainless steel can impose more serious health threat (ATSDR, 1993).

Pulmonary absorption is the major route of Ni exposure. It may be absorbed as the soluble nickel ion (Ni^{2+}) while soluble Ni compounds may be phagocytized by macrophages (ATSDR, 1988). The kidney and lung are the primary sites of its accumulation. Other organs such as the kidney, liver, heart and testis also accumulate the metal but to a lesser extent (Coogan *et al.*, 1993).

Figure 1, presents the concentration of Ni (in µg/g) for canned milk and various canned foods and drinks using AAS and photometric method. The chat below clearly indicates that the two analytical techniques (Viz AAS and photometric analysis) may not be used interchangeably for analysis of meat and fish products. The AAS values for sardine (5.11± 1.68 µg/g), canned geisha (5.70±0.95) and corned beef (3.63±1.68 µg/g) are respectively and to a greater extend lower compared to the use of photometer which gave their corresponding values as 3.09± 1.40µg/g, 0.79± 0.29 µg/g and 1.00± 0.14µg/g respectively. The metabolism of Ni is viewed in light of it's binding to form ligand and it's transport through the body (Coogan *et al.,* 1993).Although data are not available to possibly identity which Ni compound are responsible for inducing carcinogenic response, nickel oxides and soluble Ni are carcinogenic (Coogan *et al.,* 1989). This is as a result of either genetic change such as mutation of the DNA sequence and the epigenetic changes that affect gene expression without altering DNA sequence (ATSDR, 1993). Summarily, Ni contents in canned milk are higher than those of canned alcoholic, fruit and carbonated beverages but lower, compared to those of semi solid foods, including canned Geisha, tomatoes, sardine, baked beans and canned vegetable salad (Figure 1).

CONCLUSION AND RECOMMENDATION

This present analysis showed that alloying metals contents, their eruption, leaching and movement into food is critical for estimating the level of metals in semi- liquid food drink. Low pH and high conductivity resulting from increased CO_2 contents, low oxygen accompanied by alkalinity or high oxygen content in acidic medium, high temperature during processing and storage e.t.c are combined factor affecting the attenuation of heavy metals. A comparative study also revealed that the level of metals in canned milk exceed, to a greater extent, the corresponding uncanned products. The low electrical conductivity values reported in this work shows its insignificance in the metal transport .In view of this deductions, it may be necessary for milk manufactures to avoid the use of low pH or acidic water avoid excessive heating, stored and transported within favorable temperature range, reduced shelf life to avoid oxygen intake by rusted cans, use of internally lacquered cans for packaging ,use of materials made up of glass, paper and polymers, else, powdered or uncanned dairy products may be preferred.

Table 4: Comparing some Heavy Metal Concentration for (a) Canned and (b) Uncanned milk products Marketed in Nigeria.

samples	Toxic metals concentrations($\mu g g^{-1}$)						
	Cd	Co	Cr	Cu	Ni	Pb	Zn
(a)	0.02±0.008	1.61±0.21	1.47±0.73	1.62±0.31	1.64±0.66	1.12±0.48	1.75±0.29
(b)	0.006±0.003	0.09±0.05	0.01±0.01	0.33 ±0.31	0.05±0.03	0.11±0.08	1.54±1.2

Sources/Key: (a)-current work,(b)-uncanned Diary products by Onianwa *et al.,* 1999.

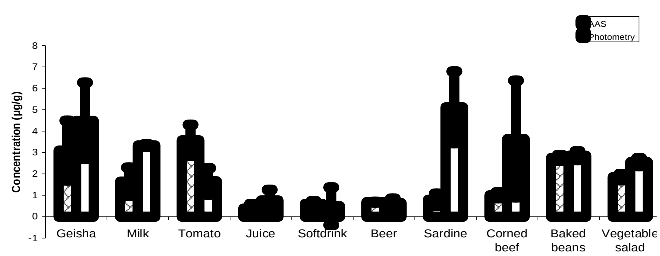

Fig. 1: Comparison of nickel in canned milk and other canned foods and beverages.

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Corresponding Author:
Dr. Itodo Udoji Adams
Department of Applied Chemistry,
Kebbi state University of Science and Technology,
P.M.B 1144, Aliero, Kebbi state
Nigeria
E-mail: itodoson2002@yahoo.com
TEL: +2348073812726, +2348039503463

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