QUANTITATIVE SPECIFICATION OF POTENTIALLY TOXIC METALS IN EXPIRED CANNED TOMATOES FOUND IN VILLAGE MARKETS

[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
itodoson2002@yahoo.com

Abstract: Varieties of expired canned tomatoes were pre-treated using standard digestion methods and were analysed for heavy metals. Cr, Pb, Cd, Fe, Ni, Co, Zn, Mg, Cu, AI and Mn were determined using Atomic absorption spectroscopy and photometry techniques. Mg, Mn, Co and Pb presented higher concentration values ranging from 32.18± 9.25; 4.35 ±1.60; 2.62 ±1.76 and 2.82 ±0.53 μgg^{-1} respectively. Unlike the Cd contents, Cr and Pb concentration were above the threshold limit values (TLV) of 2.0μgg^{-1}. The levels of metals for some of the canned foods exceed that of their corresponding uncanned products reported in literatures. Physicochemical variables of the brands were also estimated as 76.4 ±3.85 and 3.20± 1.09 % for moisture and ash contents respectively. The arrays of health implications of heavy metals computed in this work will at a glance access the roles of excessive and prolonged intake of such foods.

Key words: canned tomato, toxic metals, AAS, Photometry. [Nature and Science. 2010;8(4):54-59]. (ISSN: 1545-0740).

1. Introduction.

Knowledge of transport and accumulation of potentially hazardous metals in the ecosystem forms the central theme of canned food contamination by heavy metals. Heavy metal is a term, given to the group of metals and metalloids with atomic density greater than 5g/cm^3, usually associated with pollution and toxicological problems (Abdulrahman and Itodo, 2006). ATSDR,(1993), stated that "heavy metals" are a group of metals and semimetals associated with contaminations and are potentially toxic. Based on these definitions and observations, heavy metals are therefore classified as essential (if they play basic role as components of vital biochemical or enzymatic activities in human body e.g Fe, Mn, Mo, Cr, V, Zn) and as non-essential (if the metals are classified as with no biological, chemical and physiological importance in man (Itodo *et al*.,2009). The role played by industrial processes and emissions cannot be over emphasized. 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 soil is the main source of metals for plants. These metals readily occur in mining areas. Other sources of these metals are natural occurrence such as earthquake, volcanic eruption, and mans activities including dumping of wastes and agricultural activities (pesticides, herbicides etc) are contributing factors (Ademoroti, 1995). Pollution of streams and rivers through agricultural effluent discharges are sources of polluting the water bodies (Fodeke and Fisher, 1989). 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 (ATSDR, 1993). When the concentrations of the metals are beyond the tolerable limit, they become toxic. The tolerable limit of some metals in drinking water given in mg/l are 0.01, 0.001, 0.003, 3.00, 0.01, 0.05, 0.05, and 1.2 for Hg, Cd, Zn, Sn, Se, As, Cr(vi), and Cu respectively (WHO, 1971). Others are Fe 0.3 µg/g, Mn (0.1-0.5mg/l) WHO values (Ademoroti, 1995).

Table 1: Some heavy metals and their target organs in man.

Heavy Metals	Target Organs	Organ screened for Medical test
Aluminum	Bone, brain, Kidney and stomach	Blood, Urine, hair, faces and fingernail
Arsenic	Most organ of the body, especially Lungs, skin, gastrointestinal system	Urine, hair and finger nails
Cadmium	Brain, heart, blood vessel, kidney and lungs	Blood, urine.
Lead	Bones, brain	Blood, urine and hair
Copper	Lungs, skin and gastrointestinal tract, kidney and bones	Blood, urine, hair and finger nails
Mercury	Gastrointestinal tract, Brain, kidney and lung	Urine, blood, hair and finger nails

Sources: Abdulrahman and Itodo, 2006; ATSDR, 1993; Itodo *et al*., 2009.

Food canning implies the storing of food in airtight containers. The food is preheated to bring about the destruction of organisms .The lethal effect of heat on micro organism has been used for food preservation long before the microbial causes of food spoilage was discovered (Ngoddy and Ihekomonye, 1992).Canning of food product is the sealing of the food products after heat treatment. Canning became necessary for the following reasons: To free the food from micro organism capable of causing spoilage, or which is of public health significance e.g *Clostridium botulinum.*To keep the product clean and produce a barrier against dirty and other contaminants. It is a means of preserving and circulating excess food produced over a long period of time.Finally, perishable foods of economic values are better secured in sealed cans for import and export practices or distributions (Ngoddy and Ihekomonye, 1992).

Chemistry of Tin Plates Canning

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 acids ,citric, tartaric and oxalic acids (Steve and Tony, 2003) Reactions involving the reducing properties of tin can also occur. Therefore, the bioavailability of potentially toxic tin in food depend 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 and Tony, 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 (Itodo *et al*., 2009). This work was embarked upon to estimate the heavy metal concentration of various canned tomatoes marketed in villages within Nigeria for the purpose of: Providing data for future compilation of Nigerian food consumption table and for use by the Nigerian Standard Organizations and regulatory bodies.

2. Materials and Methods

Five varieties of canned tomato products were randomly bought from villages around Sokoto town. The considerations for sampling were manufacturing dates, place of manufacture, net weight of sample, company and brand names (not disclosed), NAFDAC registration numbers, ingredient and other information provided in Table 2 below.

Table 2: *Sampling and Nutritional Data of Various Canned Tomatoes Nov., 2005.*

Tomato Samples	Net wt.	Man. Date	Exp. date	Shelf life (months)	Food duration in cans	Ingredients	NAFDAC Number
C1	70g	June 2003	June 2005	24	5 month	Tomato, salt	01-5188
C2	70g	May 2004	April 2005	12	6 month	Tomato, salt	NS
C3	70g	May, 2003	May, 2005	24	6 month	Tomato, salt	NS
C4	70g	June, 2003	June 2005	24	5 month	Tomato, salt	NS
C5	70g	Dec. 2003	Dec. 2004	12	11 month	Tomato, salt	NS

Methods by AOAC, (1990); Abdulrahman and Itodo,(2006) and Fodeke and Fisher,1998 were modified and adopted as described below for sample treatment prior to analysis.

Nitric Acid – Hydrogen Peroxide (HNO_3/H_2O_2) Method

Already washed and dried digestion tubes were weighed and labeled to ± 0.5g. The samples were opened and the contents were homogenized after which 3 ± 0.01g samples were accurately weighed out into each digestion tube. The samples were first acidified with 2M HNO_3 and swirled to mix properly before evaporating to dryness. 25 cm^3 concentrated HNO_3 was added to the residue in the digestion tube and was heated to boiling. Addition of 25 cm^3 conc. HNO_3 was repeated with small quantity of H_2O_2. The digestion was completed by repeating the procedure until the content in the tubes became brown, pink or colorless. 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. (Ademoroti 1996).A Unicam 969 AAS was set up according to manufacturers' 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})

Nitric Acid – Sulfuric Acid (HNO_3-H_2SO_4) Method

The homogenized samples were weighed into the digestion tubes. 10 cm^3 conc. H_2SO_4 and 5 cm^3 conc.HNO_3 were added. The sample was digested and its volume was reduced to 2cm^3. The digestion was continued until the solution was colorless. This ensured the removal of all HNO_3. Sample was allowed to cool and 15 cm^3 of water was added with gentle swirling. 1M NaOH was added dropwise until a pink tinge, brown or colorless solution was produced. The solution was filtered using a Whatman filter paper No.42 followed by dilution to the mark in a 25 cm^3. Volumetric flask.

Procedure for Photometric Analysis

The machine (Windaus L.F. 2400 photometer) was 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 Discussions

Physicochemical Parameters: Table 3 presents the physicochemical variables for the sampled canned tomato. This is to appreciate the role of certain parameters that could possibly enhance the delaminating of tin coatings and subsequently, its detinning. Results on table 3 indicates the acidic nature of the products (mean pH value of 3.69 ± 0.32) and high moisture contents (76.4± 3.85 %),which could induce tin plate corrosion when combine with factors like storage temperature, air space in poorly sealed cans, and protein content (8.90 ± 2.17%) which could be responsible for content denaturing (Ngoddy and Ihekomonye, 1992)

Table 3. pH, Conductivity ,Protein, Moisture, Ash and Organic Matter Content of Canned Tomato Products

Canned Tomato Products	Physicochemical Variables					
	pH	Conductivity (µs/Cm)	Protein content (%)	Moisture content (%)	Ash Content %	Organic solid %
C1	4.10	1.00	10.38	74.00	2.00	24.00
C2	3.70	1.00	9.63	78.00	4.00	18.00
C3	3.40	1.00	9.56	76.00	4.00	20.00
C4	3.36	1.00	5.06	82.00	2.00	16.00
C5	3.92	1.00	9.87	72.00	4.00	24.00
Mean	3.69	1.00	8.90	76.4	3.20	20.40
±	±	±	±	±	±	±
S.D	0.32	0.00	2.17	3.85	1.09	3.58

Metal Analysis: The results of determination of metals (µg/g) are presented in Tables 4. Data generated were presented as mean ± standard deviation. These results were compared with those of selected canned products using histogram of the frequency distribution (Fig.1). From analysis, sample,C1 has the highest mean value of iron content of 4.30μgg^{-1} and 9.50 μgg^{-1} using AAS and photometric analysis respectively. Metals such as Cd and Pb in any concentration can pose health hazards. On the other hand, Cr, Cu, Fe, Zn and Mn are essential for human health. However for these metals to be essential, there are allowed levels for adequate dietary intake. For adults, the intake can range from 0.50 – 2.00µg Cr(iii), from 1.2 – 3.0 mg (Cu) from 10.0 – 50.0mg (Fe), from 5.0 –22.00mg (Zn) and 2.0 – 20.0mg Mn. (WHO, 1996). Cr (iv) penetrate cell membrane while Cr (III) does not. Thus, Cr(IV) may cause genotoxic effect and cancer whereas Cr(III) cannot (WHO, 1996). The mean range for values of Cd contents (0.04± 0.02µgg^{-1} using AAS and 0.05 ± 0.32 µgg^{-1},using photometer) is low compared to that of any other metals analysed. Cadmium concentration is usually low in canned food (Kent *et al.,* 2003). Cd concentration could be traced to contaminated waste water into river with subsequent flow through the food chain.

The lead content in canned food depends on the method used to seal the can. A better option is the use of welded or lacquered cans with low lead content (Kent *et al.,* 2003). Mean lead value (2.82 ± 0.53 µgg^{-1}) was obtained for tomato products. Its availability could be linked to contamination of food by lead when tomato is cooked in casserole vessels before canning (Kent *et al.*, 2003). A blood lead level greater than 1.0µg/cm^3 is dangerous to health (Adekunle, 2003).

Table:4. Concentration of Heavy Metals in Various Canned Tomato Products

HEAVY METAL CONCENTRATION (µgg^{-1})															
	(I) AAS								(II) Photometric Analysis						
Canned tomato	**Cr (i)**	**Pd (i)**	**Cd (i)**	**Fe (i)**	**Ni (i)**	**Co (i)**	**Zn (i)**	**Mg (i)**	**Cr (ii)**	**Pd (ii)**	**Cd (ii)**	**Fe (ii)**	**Ni (ii)**	**Cu (ii)**	**Al (ii)**	**Mn (ii)**
C1	3.15	3.35	0.03	4.30	4.40	3.90	0.90	32.59	1.25	4.00	0.85	9.50	1.85	5.25	0.85	6.00
C2	5.55	1.95	0.4	3.80	2.95	3.80	2.70	26.70	1.20	4.25	0.50	5.50	1.25	3.00	0.55	5.00
C3	3.90	2.80	0.09	3.85	4.10	7.00	3.45	47.00	0.85	6.25	0.85	5.50	1.15	2.50	0.95	5.25
C4	3.05	3.05	0.06	3.40	2.70	2.85	2.65	32.15	0.40	5.60	0.10	2.75	2.66	2.75	0.20	2.00
C5	3.50	2.95	0.06	1.95	3.70	2.55	5.70	22.55	0.50	6.88	0.40	4.00	1.35	3.50	0.55	3.50
Mean ± S.D	3.83 ± 1.01	2.82 ± 0.53	0.04 ± 0.02	3.46 ± 0.90	3.57 ± 0.73	2.62 ± 1.76	3.08 ± 1.74	32.18 ± 9.25	0.85 ± 0.40	5.40 ± 1.25	0.54 ± 0.32	4.81 ± 2.53	1.65 ± 0.62	2.09 ± 1.10	0.62 ± 0.29	4.35 ± 1.60

Comparative study.

Figure 1 presents the amount of Cr (in µg/g) for canned tomatoes as compared to those for various canned foods and drinks using AAS and photometric method. The AAS result obtained for tomato (3.38±1:01µgg^{-1}) is by far higher than those of others, especially canned drinks (0.52 ±0.25 to 0.86± 0. 56 for juice and beer respectively

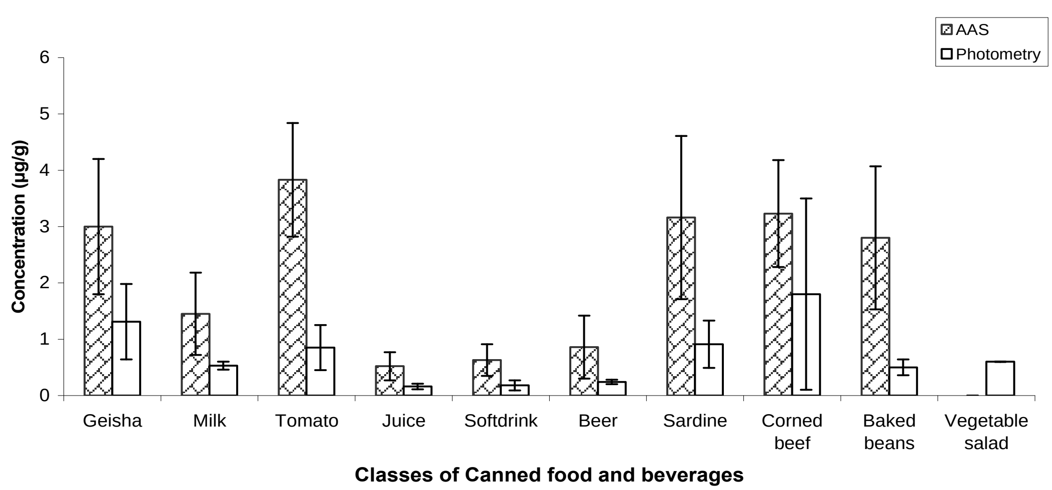

Figure 1: The concentration of Chromium in canned tomatoes as compared to various canned foods and beverages

The investigated products in this work have uncovered the fact that canning of semi – solid food and drinks is a menace, with an usually higher concentration of the toxic metals (Mn, Pb, Cd and Cr) especially when the cans are not lacquered. The researcher is uncomfortable with this high level. Therefore the contents of the containers need be checked by appropriate government regulatory bodies. Food manufacturers should avoid the use of acidic water with low pH, such foods are better bottled or paper packaged than canned. We also recommend that;

- Excessive heating and lead – soldering should be avoided.
- Shelf life should be reduced to avoid oxygen intake by corroded container,
- 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.

A critical observation of the results also revealed that metals originating from mined products and their corrosion and leaching into food is critical for assessing semi – liquid food and beverages. In the same fashion, the attenuation of heavy metals and their concentrations in canned food varies depending on the type and origin of food, pH of the medium, oxygen and carbon dioxide concentration in the headspace, quality of the inside lacquer coating of cans, storage place, temperature.

Acknowledgements:

Authors are grateful to the Department of Pure and Applied Chemistry, Usmanu, Danfodiyo University, Sokoto and to NARICT, Zaria for AAS Analysis.

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

REFERENCES

1.Abdulrahman F W , Itodo AU. Canned fish poisoning: High level of some toxic metals. Medical and Pharm .sciences 2006; 2(1):10-14.

2.Adekunle J, Ndahi J, Owolabi D. level of some Hazardous trace metal and simulated blood lead from high way soil of South – west Nigeria. International Journal on Environmental issue 2003;1 (1): 44-48.

3.Ademoroti CMA. .Environmental Chemistry and toxicology". 1st Edn. Fodulex Press Ltd Ibadan 1994; 61-67.

4.Alka S. Environmental Biochemistry A Textbook of Medical Biochemistry Brothers Med. Pub. Ltd New Delhi. 2000; 444-467.

5.AOAC.- Association of official Analytical Chemists. Official Methods of Analysis" 15th edn. Washing D.C, USA 1990; 69-88.

6.ATSDR - Agency for Toxic Substances and Disease Registry. Toxicological profile for Heavy Metals. US Department of health and Human Service 1993. Retrieved on 10/11/2004 from http//www.atsdr.com

7.Fodeke V, Fisher A. Studies on Heavy Metal Contamination of Sarotheradon (Ruppel from Lagos lagoon Journal Nigeria Natural science1989; 4 (1 and 2): 46-52.

8.Itodo .AU, Abdulrahman FW, Happiness UO, Abubakar MN. corrosion impact on the leacheability of heavy metal ions in canned juices and beverages marketed in Nigeria . Research in Sc.,Edu,Info. And Comm tech. 2009; 1 (1),164

9.Kent C. Canned Fruit. 2003.Rretrieved on 30/10/04 from www.tradingstrandard.gov.uk.

10.Steve B, Wallace T. Tin in Canned Food. Food and Chemical Toxicology 2003; 41: 1651- 1662.

11.WHO – World Health organization. "Health criteria other supporting information in: Guideline for drinking water quality, Geneva 1996 ; 2 (1):31- 388.

4/02/2010