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DETERMINATION OF THE LEVELS OF TRACE ELEMENTS IN SOME CANNED FOODS

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SEPTEMBER 2009

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NIGERIA

SEPTEMBER 2009

DECLARATION

I declare that the work in the thesis entitled “DETERMINATION OF THE LEVELS OF TRACE ELEMENTS IN SOME CANNED FOODS” has been performed by me in the Department of Chemistry under the supervision of Dr. C. E. Gimba (Chairman), Dr. O. Turoti, Dr. J. A. Kagbu and Dr. A. Uzairu.

The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this thesis was previously presented for another degree or diploma at any University.

UMAR, ZUBAIR MUHAMMAD		**September 14, 2009**
Name of Student	**Signature**	**Date**

CERTIFICATION

This thesis entitled:

DETERMINATION OF THE LEVELS OF TRACE ELEMENTS IN SOME CANNED FOODS By **UMAR, ZUBAIR MUHAMMAD**

meets the regulations governing the award of the Degree of **M.Sc (Analytical Chemistry)** of **Ahmadu Bello University, Zaria** and is approved for its contribution to scientific knowledge and literary presentation.

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(Head of Department)

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Prof. S. A. Nkom **Date**
(Dean of Post Graduate School)

DEDICATION

This work is dedicated to

My Late Father, Mallam UMAR MUHAMMAD (MARAFA TSARAGI),

My Late Mother, Mallama FATIMA UMAR

and to

All Who seek after The Truth.

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ABSTRACT

X–Ray Fluorescence analytical technique (XRF) was employed for the screening of samples of canned sardine fish and canned tomato pastes for the concentration levels of trace elements in them. The results obtained revealed the presence of Br, Cu, Fe, Nb, Ni, Zn and Zr in the two canned sardine fish samples while in the four brands of canned tomato pastes, As, Br, Cr, Cu, Fe, Pb Ti, V and Zr were detected.

All the elements detected showed concentration levels that are very high and far above the maximum limits set by most Countries, Health Agencies and International Organisations. This implies that their level of safety to humans is low and can constitute a threat to human health. It is therefore important to continuously monitor these products and their consumption since they are widely consumed in Nigeria.

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ABBREVIATIONS

ABU: Ahmadu Bello University, Zaria.

ADI: Acceptable Daily Intake

ATSDR: Agency for Toxic Substances and Diseases Registry, USA

CAOBISCO: Association of Chocolate, Biscuit and Confectionery industries of the European Union

CEH: Centre for Ecology and Hydrology, UK

CERT: Centre for Energy Research and Training

CPUT: Cape Pensula University of Technology, South Africa

EC: European Communities (Commission of European Communities)

ED-XRF: Energy Dispersive X-Ray Fluorescence

FAO: Food and Agricultural Organisation of the United Nations

GTF: Glucose Tolerance Factor

HPA: Health Protection Agency, UK.

NAA: Neutron Activation Analysis

NAFDAC: National Agency for Food and Drugs Administration and Control, Nigeria

N.D.: Not Detected

N.F.: Not Found

N.S.: Not Stated

NZFSA: New Zealand Food Safety Agency

OSHA: Occupational Safety and Health Administration USA

PTWI: Provisional Tolerable Weekly Intake

RDI: Reference Daily Intake

SF: Sardine fish

TDI:	Tolerable Daily Intake
TP:	Tomato paste
UK:	United Kingdom
UKFSA:	United Kingdom Food Standards Authority
UOI:	University of Ioannina, Greece
USA:	United States of America
USFDA:	United States Food and Drug Administration
WD-XRF:	Wavelength Dispersive X-Ray Fluorescence
WHO:	World Health Organization
XRF:	X-Ray Fluorescence

Chapter 1: INTRODUCTION

Natural as well as increasing industrial and human activities worldwide have lead to transfer of trace elements amongst other components into our environment. These activities include:

1. Mining, extraction, refining and distribution of mineral substances from their natural deposits;
2. Agricultural activities like irrigation, application of agro-chemicals and fertilisers;
3. Industrial and municipal/domestic wastes; and
4. Natural processes like volcanic eruptions, erosions and flood.

These activities and processes could lead to the discharge, distribution and concentration of these chemicals into especially the water, soil and air environments and consequently into the food chain [Milacic and Kralj (2003), Tahan *et al* (1995), CAOBISCO (1996)].

Some of these elements get accumulated in the body tissues of marine animals (in water) and crops (which take the elements in from the soil, water and the atmosphere). Thus an abundance of a certain trace element in the environment may result in a greatly increased level of that element in plant or animal products [CAOBISCO (1996)].

Trace elements are present in all foods in varying proportions. The extent of their presence in two brands of canned sardine fish and four brands of canned tomato pastes is the focus of this research work.

1.1 Statement of the Problem

Concerns about the quality and safety of foods we eat has been growing in view of reports of poisoned or contaminated foodstuffs and presence of toxic trace elements as well as elevated concentrations of the essential trace elements that may be part of such foods or added to them.

In fact, food has been identified as the primary means of exposure of the general population to chemicals, apart from occupational and incidental means. Instances of poisoning as a result of food consumption include: the 1965 Minamata and Niigata diseases in Japan which was linked to methyl mercury contaminated fish consumed there (in Japan) as the causative agent; in Iraq in 1972/73, mercury treated wheat grains consumed there was reported to have affected 6,500 people and to be responsible for at least 459 hospital deaths; the Itai-Itai disease with bone damage in Japan was attributed to the consumption of cadmium contaminated rice [Lindsay (1981), Hamilton (1979), CAOBISCO (1996)].

Recently, in Nigeria too, there have been reports of ill-health, some of which resulted in deaths, after consumption of certain foodstuffs (in particular, beans) suspected to have been treated with pesticides or preserved in containers that may have earlier been used to package chemicals or poisonous substances.

These developments, amongst several unreported cases, are indeed matters of serious concern and that is what forms the basis of this research.

1.2 Trace Elements

1.2.1 Definitions

Trace elements have been defined in several ways. Some of these are:

(a) Elements that are present at low concentrations (mg/kg or less) in most soils, plants, and living organisms [He *et al* (2005), Duffus (2002), Florkin and Stortz (1971)];

(b) Elements that are present in a given substance in amounts below 50ppm [CPUT (2005)].

(c) Elements in a sample that have an average concentration of less than100ppm atoms [en.wikipedia.org (2006)].

Trace elements are most often called trace metals since virtually all of them are metals. Majority of them are also referred to as heavy metals [He *et al* (2005)] as in their standard state, they have a specific gravity (density) of 5gcm^{-3} or more [Duffus (2002), CAOBISCO (1996)]. The terms trace elements, trace metals, and heavy metals have thus been used interchangeably as appropriate in this work.

Trace elements include: aluminium (Al), antimony (Sb), arsenic (As), boron (B), bromine (Br), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iodine (I), iron (Fe), lead (Pb), manganese (Mn), mercury (Hg), molybdenum (Mo), nickel (Ni), nobium (Nb), selenium (Se), silicon (Si), thallium (Tl), tin (Sn), titanium (Ti), vanadium(V), zinc (Zn) and zirconium (Zr).

1.2.2 Classification

Trace elements can be classified into:

(a) Essential nutritive elements. e.g. Cu, I, Fe, Mn, Mo, Ni, Se and Zn.

(b) Non-nutritive, non-toxic elements. e.g. Al, B, Sn.

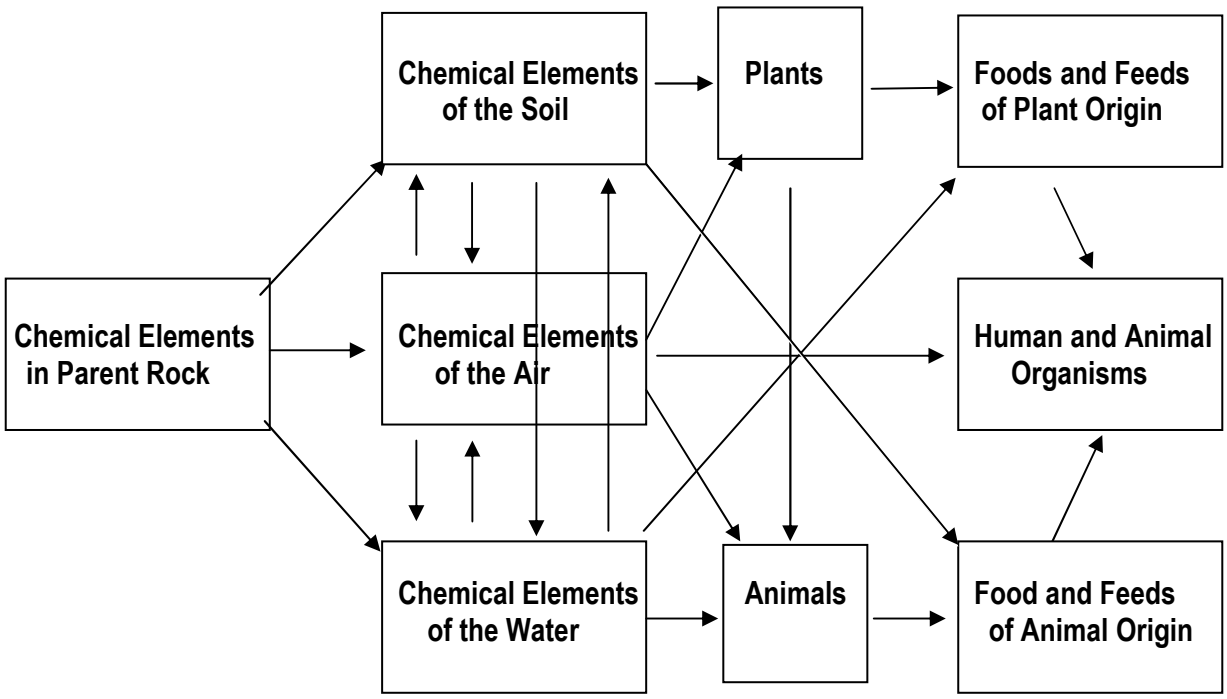
(c) Non-nutritive, toxic elements. e.g. Sb, As, Cd, Pb, Hg. [CPUT (2005)].

Trace elements have also been classified into: Those essential for higher animals; those possibly essential; and the non-essential [Underwood (1977)]. An element is considered essential if its deficiency consistently results in impairment of function from optimal to sub-optimal [Nicholas and Egan (1975)].

1.2.3 Sources

Trace elements occur in different chemical compounds having varying solubility, depending upon the chemical and physical environments [Nicholas and Egan (1975)]. Generally, the abundance of trace elements in foods is related to their abundance in the environment [CPUT (2005)].

The biogeneous movement of chemical elements in the biogeochemical nutritional chains can be represented as shown in Figure 1



[Mills (1970)]

Figure 1: Movement of Chemical Elements in the Biogeochemical Nutritional Chain

Contamination of food products with metals can also occur due to pick up of metals from equipment, processing or packaging materials.

Sources of some specific trace elements that find their way into foods one way or the other are as in Table 1

Table 1: Sources of some Trace Elements

Trace Element	Common Sources
As	Combustion, agrochemicals, veterinary products.
Cd	Zinc smelters, battery industry, pigments, solders, cigarette smoke, porcelain.
Cr	Plating, pigments, tanning, dyeing.
Cu	Industrial use, agrochemicals.
Hg	Mining, volcanic activity, chloroalkali, electrical industry, agrochemicals, dentistry, paper industry.
Mn	Agrochemicals, paints, red bricks, glass cleaners.
Ni	Alloys, plating.
Pb	Natural, combustion, paints industries; Solders, accumulators, anti-rust agents, cigarette smoke, porcelain.
Sb	Paints, pigments.
Sn	Canning.
Tl	Lead smelting, rodenticides.
Zn	Plating.

[Jarup (2003), Pickford (1981), NZFSA (2006), CAOBISCO (1996), health.enotes.com (2007)]

1.3 Canned Foods

To have all foods available in nearly its complete and natural form retaining virtually all its essential mineral constituents intact with minimal loses, foods are preserved by amongst other means, salting, freezing, oiling, smoking, frying and canning. Of all these, canned foods can remain stable and suitable for consumption for a relatively longer period of time, thus canning has become one of the most acceptable means of preserving foods.

Canning can be a safe and an economical way to preserve food quality, despite possible loses or alteration in the nature of food products during processing. Foods are canned in glass jars, paper packs, plastics and metal containers with each requiring some special form of sealing [Kocak *et al* (2005)].

Canned foods are valuable commodities worldwide [Kocak *et al* (2005)]. Many foods begin to lose their essential nutrients and even deteriorate immediately after harvesting. While some can remain edible and safe for days, weeks or even months, some begin to deteriorate almost immediately if not consumed or processed and preserved appropriately.

In addition to trace elements that are part of or accompany the foods from source, canned foods may take up metals from their container, tin and iron from tin plate, tin and lead from the solder [CPUT (2005)]. Tin plate used for most metal cans is a light gauge, steel sheet or strip, coated on both sides with commercially pure tin and has been used for well over a hundred years as a robust form of food packaging. Worldwide, about 80,000million cans are used for food packaging [Blunden and Wallace (2003)].

Canned foods accumulate more tin when stored for several months and corrosion is accelerated at temperatures of about 40^{o}C [Joint FAO/WHO CODEX Committee (2004)].

In this study, two types of foods canned in tin plates: one of animal origin (sardine fish – two brands) and the other of plant origin (tomato paste – four brands) have been chosen. They are widely consumed in Nigeria.

1.3.1 Sardines

Sardines are found in temperate waters and can grow up to as long as 12 inches. They travel in very large "schools" feeding on tiny invertebrates and crustaceans [www.acornnaturalists.com (2006)]. Sardines used to be abundant just off the coast of Sardinia, an island in the Mediterranean, hence the name "Sardine". It is also known as the Atlantic or Sea Herring, "Pilchards" [www.wholeHealthMd.com (2006)].

Scientifically, sardine is classified as follows:

Kingdom	*Animalia*,
Phylum	*Chordata*,
Class	*Actinopterygii,*
Order	*Clupeiformes,* and
Family	*Clupeidae.*

There are several types of Genus (e.g. *Escualosa, Dussumena, Sardinops*) and Species (e.g. *Elongata, Elopsoidas, Sagax*) [www.answers.com (2006), en.wikipedia.org (2006)].

The sardine was first canned at the beginning of the 19th century when Napoleon recognised that there was a need to preserve food, and the Sardine was the first fish

to be preserved in oil or tomato sauce. In fact it is one of the world's first canned foods [www.wholeHealthMd.com (2006)].

Sardine is packed full of important nutrients such as Omega-3 fatty acids, protein and calcium. Like other cold water fish, sardines contain the highest amounts of heart-healthy Omega-3 fatty acids. It is also rich in phosphorous, iron, potassium, vitamin B_6, and niacin. Vitamin B_{12} and selenium are also available at μg level [Ikem and Egiebor (2005), www.wholeHealthMd.com (2006)].

Fish and other aquatic life forms are constantly exposed to chemicals in polluted and contaminated waters. Crustacea, a meal of sardines, accumulate metal ions from the ambient seawater [CPUT (2005)]. Trace metals may also get into fish from discharges into water systems like rivers, lakes, seas and oceans.

1.3.2 Tomatoes

Tomato, (derived from *tomatl* (Nahuatl language) later *tomate* (spanish)), *Lycopersicum esculentum* is an edible, fleshy and usually red fruit (or vegetable) of a vine native to South America. It is one of the newest plants to be used on a large scale for human food. It was commonly regarded as poisonous being a member of *Solanaceae* (nightshade) family and only within the last century has it become recognised as a valuable food. Indeed, all parts of the plant but the fruit are toxic [www.answers.com (2006)]. Numerous varieties (ranging from the small cherry tomato, globe, plum, to the large beefsteak tomato) in various sizes, shape and colour are cultivated worldwide.

Technically, tomato is a fruit, but commonly considered a vegetable because of its uses [www.answers.com (2006)].

The tomato is classified as follows:

Kingdom	*Plantae*,
Subkingdom	*Tracheobionta*;
Division	*Magnoliophyta*;
Class	*Magnoliopsida*;
Subclass	*Asteridae*;
Order	*Solanales*;
Family	*Solanaceae*;
Genus	*Solanum*;
Species	*S. Lycopersicum* [www.answers.com (2006)].

Canned tomatoes are available in various forms including [www.answers.com (2006)]:

1. *Canned tomato paste* – consists of tomatoes that have been cooked for several hours, strained and reduced to a deep red, richly flavoured concentrate. E.g. *De Rica* Tomato Paste.
2. *Canned tomato puree* – consists of tomatoes that have been cooked briefly and strained, resulting in a thick liquid. E.g. *Heinz* Tomato Puree;
3. *Tomato sauce* – is a slightly thinner tomato puree, often with seasonings and other flavourings added so that it is ready to use in various dishes or as a base for other sauces. E.g. *Heinz* Tomato Sauce.

The first to commercially can tomatoes was Harrison Woodhull Crosby in Jamesburg, New Jersey [www.answers.com (2006)].

Tomatoes are rich in vitamin C and contain appreciable amounts of vitamins A and B, potassium, iron and phosphorous. A medium sized tomato has about as much

fibre as a slice of whole-wheat bread and only about 35calories. From its seed, tomato-seed oil and tomatine (an antibiotic) can be extracted [www.answers.com (2006)]. Tomato consumption is believed to benefit the heart. Lycopene, one of nature's most powerful antioxidant present in tomatoes has been found to be beneficial in preventing prostate cancer [www.answers.com (2006)].

1.4 Aim and Objectives of this Research

The primary aim of this research is to determine the concentration levels of trace elements in some canned foods to achieve the following objectives with reference to canned sardine fish and canned tomato paste samples:

1. To assess the health significance associated with the consumption of a particular trace element in these foods;
2. To indicate the possible presence of potentially toxic substances in these samples;
3. To show whether or not the restrictions placed on the use of toxic substances as additives in the production and/or processing of these foods are being met in practice;
4. To assess whether there is the need to introduce new legislations or to revise existing ones as they affect these foods;
5. To indicate the level of safety of these canned foods.

To achieve these objectives, the samples would be analysed using X-Ray Fluorescence Spectrometry (XRF). It is available at the Centre for Energy Research and Training/Ahmadu Bello University (CERT/ABU), Zaria.

1.5 Justification of this Research

Foods pick up trace elements from either the environment during production or from processes of handling and preservation such as canning [Pickford (1981)]. Some trace elements such as mercury, lead, arsenic and cadmium are harmful even at low concentrations and can cause damage to the basic human systems (cardiovascular, renal, gastrointestinal, nervous, etc), while others such as copper, iron, zinc and manganese which are regarded as essential do produce toxic effects at very high concentration levels [Tuzen (2003), Cid *et al* (2001), Pickford (1981), CAOBISCO (1996)] more than what the body requires for normal functioning of its systems.

The concentration levels of trace elements in foods and the amount of food consumed determines the level of intake of such elements into our body systems [Ikem and Egiebor (2005)]. Some of the trace elements, especially the toxic ones are usually persistent and not readily biodegradable [USFDA (2008)].

Therefore, there is the need for continuous study of foods to obtain information on the concentration levels of all the trace elements in them for the assessment of the safety of such foods and the associated risks to human health [Llobet *et al* (2003)] when consumed.

Chapter 2: LITERATURE REVIEW

Growing concern about the quality of food has brought about numerous investigations on the presence of essential and toxic trace elements in different foodstuffs [Milacic and Kralj (2003)].

Food has been identified as the primary means of exposure of the general population to chemicals, apart from occupational and incidental means as well as gaseous pollutants. For instance, methyl mercury contaminated fish consumed in Japan was identified to be the causative agent in the 1965 Minamata and Niigata diseases; mercury treated wheat grains consumed in Iraq in 1972/73 was also said to have affected 6,500 people and to be responsible for at least 459 hospital deaths; the Itai-Itai disease with bone damage in Japan was attributed to the consumption of cadmium contaminated rice; amongst several unreported cases [Lindsay (1981), Hamilton (1979), CAOBISCO (1996)]. These discoveries have made it imperative to obtain data on the elemental constituents of the foods we eat and their health implications.

The exposure to trace elements in foods may come from:

1. concentration of environmental levels of trace elements by many organisms
2. contamination of food by processes such as canning [Pickford (1981)] as well as some activities of man.

Food is a constant source of toxic trace elements which accumulate in different parts of the human body and cause damage in many of its basic systems (renal, cardiovascular, gastrointestinal, endocrine, nervous, etc). While mercury, lead, and cadmium are considered to be the most dangerous metals even at low

concentrations, other elements such as copper, nickel, chromium, zinc, iron and manganese, although considered essential, can also produce toxic effects and cause metabolic anomalies when their intake is excessively elevated [Tuzen (2003), Cid *et al* (2001), Pickford (1981), CAOBISCO (1996)].

The dietary intake of an element from food consumption is dependent on the concentration of the element in the food and the amount of the food consumed [Ikem and Egiebor (2005)]. Thus, the need for continuous assessment of the levels of all the trace elements in foods, whether toxic or not, is quite essential since some of the beneficial ones among them could have some adverse health effects at concentrations higher than the normal level required by the body especially if they are such that are not readily excreted.

2.1 Potential Health Effects of some Trace Elements

Adequate physiological functions of humans require adequate intakes of some essential trace elements. However, humans get exposed to harmful non-essential elements, apart from occupational and incidental means, through consumption of fresh and processed foods [Ikem and Egiebor (2005), Yang (2005), Ryan *et al* (2001)]. Such toxic elements which are usually persistent and not easily biodegradable [USFDA (2008)] may be biologically incorporated into items of food, trapped on external surfaces, or added as a result of manufacturing, or preparing foods for consumption [Hamilton (1979)].

A number of trace elements have received attention as both environmental contaminants, and potential health and toxicologically hazardous materials. The toxicological hazards may be due to their relative uptake and accumulation and toxicity to humans [Ryan *et al* (2001), CAOBISCO (1996)].

An outline of the potential health effects of some of the trace elements are presented below:

1. *Aluminium (Al)*: Toxicity of aluminium at elevated levels is recognised as an important factor in the Alzheimer's disease, dialysis dementia, (both are neurological malfunctions), osteoporosis, osteomalacia, (both are bone disorders) [Onianwa *et al* (1997), Burgess (1996), Tahan *et al* (1995), CPUT (2005), health.enotes.com (2007)].
2. *Antimony (Sb)*: Toxicity effects of antimony include nausea, vomiting, diarrhoea. Cumulative effects can result in heart and lung damage. Other effects include: dermatitis, headache, anorexia, tracheitis, pneumoconosis, pulmonary oedema, ulceration of nasal septum and larynx, insomnia, bloody stool, etc. [NZFSA (2006), OSHA (2006)].
3. *Arsenic (As)*: Arsenic has been associated with human cancer, anaemia, liver damage, cardiac abnormalities, dermatitis, decreased nerve conduction velocity. Acute exposure can cause lung distress and death, cardiac arrhythmia and other adverse side effects [Jarup (2003), CEH (2008), CPUT (2005), NZFSA (2006), OSHA (2006), USFDA (2008), health.enotes.com (2007)].
4. *Boron (B)*: Boron plays a role in calcium and phosphate metabolism, bone production and upkeep, nucleic acid and lignin biosynthesis, etc. An excess of it can be toxic [Burgess (1996)].
5. *Bromine (Br)*: Bromine is corrosive to human tissues. it can cause sore throat, cough, chest tightness, bronchospasm, pulmonary oedema, drooling, difficulty swallowing with retrosternal and abdominal pain and circulatory collapse. Severe cases may be complicated with haematemesis and shock. The larynx may be burned causing air way obstruction and difficulty clearing bronchial secretions.

Bromine also causes damage to organs like liver, kidneys, lungs, milt and the nervous system [HPA (2008), LENNTECH (2008)].

6. *Cadmium (Cd)*: Cadmium is a cumulative poison, frequently resulting in kidney damage (necrotic protein precipitation), Itai-Itai disease (with bone damage), reproductive deficiencies. Cadmium toxicity affects the brain, heart and blood vessels, kidneys and lungs and may cause anaemia, emphysema, lung cancer, liver dysfunction or damage, etc. It has the ability to replace zinc in the body with dangerous consequences [Kocak *et al* (2005), Jarup (2003), Abou-Arab *et al* (1996), Pickford (1981), CAOBISCO (1996), CEH (2008)]
7. *Chromium (Cr)*: Chromium(III) is an essential nutrient to humans helping the body to use sugar, protein and lipids. It is an integral part of “Glucose Tolerance Factor” (GTF) – maintaining normal glucose tolerance in organisms. Excessive amount of chromium(III) however may cause adverse health effects. The chromium(VI) is more toxic to humans and is a known carcinogen [Ikem and Egiebor (2005), Cubadda *et al* (2003), Ryan *et al* (2001), Prasad (1978), ATSDR (2006)].
8. *Cobalt (Co)*: The only known function of cobalt in humans appears to be related to its presence in the vitamin B_{12} molecule or one of the carbamides. Exposure to high levels, however, of cobalt can result in lung and heart problems, cardiomyopathy and dermatitis [Prasad (1978), Florkin and Stortz (1971), ATSDR (2006), health.enotes.com (2007)].
9. *Copper (Cu)*: Copper plays an essential role in collagen synthesis and good health but very high intake of it can cause nausea, diarrhoea, stomach cramp, kidney damage and Wilson’s disease. Deficiency leads to anaemia, hyperlipidemia. Unexcreted excess may be found deposited in the eyes [Dudek (2006),

Abou-Arab *et al* (1996), Prasad (1978), Williams (1971), ATSDR (2006), NZFSA (2006), health.enotes.com (2007)].

10. *Iodine (I)*: Iodine is essential for prevention of goitre. A deficiency results in goitre, lethargy. Its toxicity results in enlarged thyroid gland and decreased thyroid activity [Dudek (2006)].
11. *Iron (Fe)*: Iron deficiency causes anaemia, impaired immune function, fatigue, intolerance to cold temperature while excess of it gives rise to a condition of siderosis. Other toxic effects include joint diseases, enlarged liver amenorrhoea, impotence, etc. [Dudek (2006), Ikem and Egiebor (2005), Williams (1971), OSHA (2006), health.enotes.com (2007)].
12. *Lead (Pb)*: Lead is a typical cumulative poison. It is known to induce reduced cognitive development and intellectual performance in children; and increased blood pressure and cardiovascular disease in adults. Lead toxicity may cause anaemia, anorexia, brain damage, abdominal pain, convulsions, hypertension, miscarriage, tremours, renal tube nephrosis and diminished IQ (Intelligence Quotient) in children. It also damages the kidney and the reproductive system, and is responsible for encephalopathies in the central nervous system [Kocak *et al* (2005), Jarup (2003), CAOBISCO (1996), CEH (2008), NZFSA (2006), UKFSA (1998 and 1999), health.enotes.com (2007)].
13. *Manganese (Mn)*: Manganese is among the least toxic of the trace elements to mammals. It is needed for enzyme activation. However, inability to remove excess of it from the body leads to pneumonitis and the development of nervous system problems [Prasad (1978), Williams (1971), ATSDR (2006), CPUT (2005), health.enotes.com (2007)].

14. *Mercury (Hg)*: Chronic effects of mercury include tiredness, loss of appetite, weight loss. Kidney failure, muscular weakness and paralysis can result from acute intake. Mercury also damages the central nervous system and the immune system. Teratogenic effects have also been observed. Minamata and Niigata deaths in 1965 in Japan, abnormalities in newly born children also in Japan, 459 hospital deaths in 1973 in Iraq, have all been linked to consumption of food items containing mercury. It also has toxic effect on the developing foetus and it is a possible human carcinogen. [Ikem and Egiebor (2005), Jarup (2003), Hills (1997), Abou-Arab *et al* (1996), Burgess (1996), Lindsay (1981), Hamilton (1979), Florkin and Stortz (1971), CAOBISCO (1996), CEH (2008), NZFSA (2006), health.enotes.com (2007)].
15. *Molybdenum (Mo)*: Molybdenum plays a role in several enzyme reactions. Exposure to it at elevated levels causes gout-like symptoms [Dudek (2006)].
16. *Nickel (Ni)*: Deficiency of nickel leads to diminished growth and impaired normal iron absorption leading to anaemia. Nickel has been associated with allergies. It is carcinogenic and can cause respiratory problems. Ingestion of toxic levels can result in headache, vomiting, vertigo and nausea [Kirchgessner (1978), ATSDR (2006), CAOBISCO (1996), CEH (2008), health.enotes.com (2007)].
17. *Nobium (Nb)*: Nobium causes eye and skin irritation. It is retained primarily in the lungs and secondarily in the bones. It interferes with calcium as an activator of enzyme systems [LENNTECH (2008)].
18. *Selenium (Se)*: Selenium protects against liver necrosis. Deficiency of it leads to liver necrosis, muscular dystrophy and exudative diathesis, enlarged heart, poor heart function, impaired thyroid activity. Too much of nobium can cause nausea, vomiting, abdominal pain, diarrhoea, nerve damage, hair, skin and nail

abnormalities, ciirhossis, and enlarged spleen [Dudek (2006), Kirchgessner (1978), NZFSA (2006), health.enotes.com (2007)].

19. *Silicon (Si)*: Silicon is involved in an early stage of bone formation and in hastening the rate of bone mineralisation [Blunden and Wallace (2003), Kirchgessner (1978)].
20. *Thallium(Tl)*: Excessive amounts of thallium can cause hair loss, confusion, seizures, paralysis, kidney failure, heart failure and subsequently death [Burgess (1996), health.enotes.com (2007)].
21. *Tin (Sn)*: Excessive intake of tin may cause gastrointestinal irritations, diarrhoea, vomiting, nausea, anaemia, liver and kidney problems, and skin and eye irritations [ATSDR (2006)].
22. *Titanium(Ti)*: Titanium has low toxicity. However, dust inhalation of or excessive exposure to it may cause tightness and pain in the chest, coughing and difficulty in breathing. Contact with skin and eye may cause irritation [LENNTECH (2008)].
23. *Vanadium (V)*: High uptake of vanadium can cause bronchitis, pneumonia, irritation (of lungs, eyes, throat and nasal cavities), cardiac and vascular diseases, inflammation of stomach and intestines, damage to the nervous system, bleeding of liver and kidneys, skin rashes, severe trembling and paralysis, etc. [LENNTECH (2008)]
24. *Zinc (Zn)*: Zinc plays some role in growth and development, deoxyribonucleic acid (DNA) synthesis, acrodermatitis enteropathica theraphy. Its deficiency may lead to growth retardation, mental lethargy, delayed wound healing, delayed sexual maturation, and impotence, anorexia, taste abnormality, alopecia, dermatitis, hypogonadism, enlarged liver, decreased immune function, etc. Toxic effects of zinc include: anaemia, diarrhoea, fever, renal failure, reproductive

failure, nephritis, extensive lesions in the kidney [Dudek (2006), Abou-Arab *et al* (1996), Kirchgessner (1978), Prasad (1978), Halsted *et al* (1972), health.enotes.com (2007)].

25. *Zirconium (Zr)*: Zirconium has low systemic toxicity, however at high concentrations there is risk of cancer [LENNTECH (2008)].

A balanced nutrition of essential trace elements is important to assure human health. However, essential trace elements at too high or low levels can disorder the metabolism and threaten human health. The deficiency in humans mainly results from their low concentrations and bioavailability in the diet. The bioavailability of trace elements in the diet is largely dependent on enhancers and inhibitors in the food [Yang (2005)].

It is important to note that not all forms of these elements are toxic. In other words the level of toxicity of trace elements varies with the form and oxidation state(s) of the element. For instance, chromium(VI) is the toxic form of chromium; toxicity of inorganic arsenic and selenium are higher than the organic; the organic tin is the toxic while the inorganic tin is virtually non-toxic; lead and mercury are poisonous regardless of the chemical form in which they are present [Hills (1997)].

Other factors that affect the level of an element in humans include the level of exposure, sensitivity of the host, physiological and nutritional status of the host.

Although toxicity and the resulting threat to human health of any contaminant are, of course, a function of its concentration in foods, it is well known that chronic exposure to arsenic, cadmium, mercury and lead at relatively low levels can cause adverse effects. While some individuals are primarily exposed to these contaminants in the work place, for most people the main route of exposure to these toxic elements is

through the diet. Consequently, information about dietary intake to assess risks to human health is essential [Llobet *et al* (2003)].

2.2 Concentration Levels of Trace Elements in Foods

Significant advances have been made in recent years on the levels of trace elements in foodstuffs, especially through improvement in analytical methodology. Because of the very great interest in these elements, the toxic of the trace elements seem to be receiving more attention in greater details than the non-toxic elements [CAOBISCO (1996)], as have been reported in some of the literature cited below.

The typical quantities of cadmium consumed per person per day in the West industrialised societies are between 10 and 50μg and 70% of this comes from foodstuffs [CAOBISCO (1996)].

Almost all foods have inherently low level of cadmium, with the highest levels reported to occur in shellfish, meat, grain products, leafy vegetables, potatoes and other root vegetables [Ryan *et al* (2001)]. A range of 0.003 – 0.3mg/kg of cadmium has been reported. Among the foodstuffs which present a problem of cadmium concentrations are crustaceans and shellfish. Overall however, vegetables are of greater importance for human cadmium contamination. Rice and wheat contain 10 – 150μg/kg, fish and fruit, between 1 and 50μg/kg [CAOBISCO (1996)].

The highest levels of lead measured have been in seafoods, vegetables, fruits meat and grains [Ryan *et al* (2001)]. A range of 0.03 – 1.0mg/kg and even up to 10mg/kg have been found in canned foods.

Amongst all foodstuffs, it has been reported that, practically, only seafoods exhibit relatively high content of mercury [Ashraf (2006), CAOBISCO (1996)]. Values in the range 0.003 – 0.1 and up to 3.1μg/g have been observed. Vegetable foods are only very slightly contaminated with mercury, except when grown in the vicinity of emitting industrial plants.

For arsenic, the highest concentrations found in foods exist in several types of seafoods [Ryan *et al* (2001)]. A range of 0.001 – 0.1mg/kg has been reported.

The total concentration of chromium in foods is generally low, with the highest values found in acidic fruits, vegetables, meats and seafoods. A range of 0.01 – 3.0mg/kg chromium has been reported [Ryan *et al* (2001)].

In a study on seafoods also, 0.1 – 30mg/kg copper has been reported. For tin, it was 0.03 – 10 and up to >300mg/kg. The value for zinc was 1.0 – 100mg/kg [Ryan *et al* (2001)].

In many biological materials, selenium is found largely in the protein fraction. Various fish and fish products may contain more than 1μg/g selenium [Prasad (1978)].

The Iodine content of foods of marine origin is much higher than that of any other class of foodstuffs [Prasad (1978)]. Values in the range 300 – 3000ppb, on fresh basis, of iodine has been reported for the edible flesh of seafish and shellfish compared to 20 – 40ppb for fresh water fish. Likewise, values of up to 10ng/g of vanadium have been found in fish [Kocak *et al* (2005)].

Concentrations of copper and zinc in some Nigerian food items obtained from the markets in Ibadan city, Nigeria were determined. Copper levels were found to range

widely from 0.06 – 13.3mg/kg while that of zinc were 0.06 – 56.9mg/kg [Onianwa *et al* (2001)].

The trace element contents of ten canned foods marketed from Turkey revealed the following ranges in μg/g:

Cu: 2.85 – 7.77, Zn: 8.46 – 21.9, Mn: 6.46 – 18.6, Fe: 27.5 – 79.9,
Se: 0.05 – 0.35, Al: 0.93 – 3.17, Cr: 0.19 – 9.52, Ni: 0.18 – 0.75,
Co: 0.20 – 1.10. [Tuzen and Soylak (2007)].

Analysis of toxic trace elements in seafoods consumed by the general population of Malaysia revealed the following ranges in mg/kg (fresh weight): 1.42 – 5.61, 0.06 – 0.42, 4.2 – 20.6, 0.41 – 1.28 for arsenic, mercury, zinc and selenium respectively [Sarmani *et al* (1993)].

Analysis to determine the concentration of zinc, copper, cadmium, lead, nickel and chromium in some Slovenia foodstuffs was found to be in the range: 20 – 90, 0.8 – 3, <0.03, <0.2, <0.02 and <0.05 all in mg/kg respectively [Milacic and Kralj (2003)].

2.3 Concentration Levels of Trace Elements in Fish

Fish are often at the top of the aquatic food chain and may concentrate large amounts of some metals. Accumulation patterns of contaminants in fish depend both on uptake and elimination rates [Abou-Arab *et al* (1996)].

Extensive surveys have been carried out in a number of countries, to evaluate the presence of heavy metals in the aquatic biota, including fish, which can often be considered as indicators of marine pollution [Ashraf (2006), Voegborlo *et al* (1999), Sharif *et al* (1991)].

Tables 2.1 to 2.3 below show the range of concentrations in mg/kg of trace elements obtained in some earlier studies in different places for uncanned fish, canned fish (general) and canned sardine fish samples.

Table 2.1: Reported Concentration Ranges of some Trace Elements in Uncanned Fish Samples

Trace Elements	Concentration Range (mg/kg)
Cd	0.002 – 0.18
Co	0.00 – 3.29
Cr	0.00 – 14.80
Cu	0.516 – 1,005
Fe	7.46 – 163
Hg	0.00 – 2.066
Mn	0.00 – 12.81
Ni	0.635 – 5.68
Pb	0.0103 – 0.93
Sb	0.00 – 849
Zn	4.71 – 339.76

[Turkmen *et al* (2008), Uysal *et al* (2008), Uluozlu *et al* (2007), Garg and Ramakrishna (2006), Tuzen (2003), Cid *et al* (2001), Tahan *et al* (1995)]

Table 2.2: Reported Concentration Ranges of some Trace Elements in Canned Fish Samples (General)

Trace Elements	Concentration Range (mg/kg)
Al	0.45 – 1.50
As	0.00 – 1.720
Cd	0.00 – 0.69
Co	0.00 – 0.10
Cr	0.00 – 1.70
Cu	0.01 – 5.33
Fe	0.01 – 88.40
Hg	0.02 – 0.86
Mn	0.01 – 2.55
Ni	0.00 – 0.85
Pb	0.00 – 1.20
Se	0.96 – 3.64
Sn	0.04 –28.70
V	0.00 – 0.31
Zn	0.14 – 97.80

[Tuzen and Soylak (2007), Ashraf (2006), Ashraf *et al* (2006), Ikem and Egiebor (2005)].

Table 2.3: Reported Concentration Ranges of some Trace Elements in Canned Sardine Fish Samples

Trace Elements	Concentration Range (mg/kg)
Al	90 – 102
As	0.00 – 1.120
Cd	0.004 – 0.184
Co	0.00 – 0.036
Cr	0.00 – 18.90
Cu	0.50 – 1.75
Fe	0.24 – 159
Hg	0.019 – 1.30
Mn	0.01 – 15.77
Ni	0.00 – 0.156
Pb	0.00 – 25.7
Sn	0.11 – 0.78
V	0.001 – 0.312
Zn	0.06 – 21

[Ikem and Egiebor (2005), Tarley *et al* (2001), Onianwa *et al* (1997), Abou-Arab *et al* (1996), Tahan *et al* (1995)].

Concentrations of total mercury, arsenic, lead and cadmium in common edible fresh fish and shellfish from various areas of the Adriatic sea were measured. The highest values of mercury and arsenic were found in hake (0.373 ± 0.075 and 23.3 ± 3.6 respectively) and lowest in mackerel (0.153 ± 0.028 and 1.06 ± 0.29 respectively). The highest levels of lead and cadmium were found in mussel (0.150 ± 0.009 and 0.142 ± 0.017 respectively) and lowest in hake (0.007 ± 0.004 and 0.002 ± 0.001 respectively) all in mg/kg [Jure and Blanu (2003)].

These studies reveal that the levels of the essential metals in the fish samples were generally higher than the values obtained for the non-essential metals.

It has been observed that the level of contaminants in fish brands may be influenced by: the duration of exposure to contamination in water, feeding habit of the fish, concentrations of contaminants in the water column, water chemistry, uptake and elimination rates, contamination of fish during handling and processing, quality of the canned fish, shelf life of the canned fish, storage of the canned fish, the quality of the lacquer coating [Ikem and Egiebor (2005), Abou-Arab *et al* (1996), Tahan *et al* (1995)].

2.4 Concentration Levels of Trace Elements in Tomatoes

While a lot of work has been done and is still being done on fish and has been reported in several literature, not as much is available on tomatoes with respect to the concentration levels of trace elements. A few are reviewed below:

In Turkey, canned sliced tomato was reported to contain: Cd^{2+}: 0.308 – 0.318, Cu^{2+}: 0.000 – 1.968, Pb^{2+}: 0.262 – 0.372, Zn^{2+}: 3.627 – 3.777 all in mg/L. The Cu^{2+}

content of tomato salsa was also reported in the same study to be 3.074mg/L [Kocak *et al* (2005)].

Study on different kinds of canned tomatoes in Britain showed that manganese (in mg/kg), in canned tomatoes contained 0.9; canned tomato juice, 0.5 – 1.6; tomato ketchup, 1.9 & 2.2; tomato paste, puree and sauce, 2.2 – 6.1 [Wenlock *et al* (1979)].

For canned tomato paste samples collected in Ibadan, Nigeria, the range of concentrations of aluminium in mg/kg was 17.8 – 26.7 while that for tomatoes in Brazil showed 0.3 – 3.2 [Onianwa *et al* (1997)].

Analysis of transition metals conducted in Turkey on canned tomato paste samples resulted in the following: Fe: 6.8±1, Cu: 6.1±1.2, Zn: 7.4±1.1 all in mg/kg [Turker and Yuksel (1997)].

2.5 Surveillance and Regulation

The relative reckless handling of heavy metals and other trace elements and their compounds in the past can partly be explained by the fact that their effects were unknown, and the lack of any system of control over the manufacture, use, and disposal of industrial chemicals [Lindsay (1981), CAOBISCO (1996)] They however, have become a focus of public interest since the potential health effects of most of them are now known and analytical techniques have made it possible to detect them even in very small traces, down to thousandth of mg/kg.

With these possibilities, the CODEX Alimentarius is busy with preparation of standards for heavy metals in foodstuffs amongst others, since even foodstuffs

produced in completely unpolluted areas may not be entirely free of heavy metals [CAOBISCO (1996)].

Several agencies such as the Food and Agricultural Organisation (FAO), the World Health Organisation (WHO), United States Food and Drug Administration (USFDA), Health Canada, United Kingdom Food Standards Authority (UKFSA), New Zealand Food Safety Agency (NZFSA), etc, provide guidelines on the intake of trace elements by humans. The agency in-charge of foods regulation in Nigeria is the National Agency for Foods Drugs Administration and Control (NAFDAC).

While the Joint FAO/WHO Expert Committee on Food Additives and Contaminants recommends Permissible Tolerable Intakes (Provisional Tolerable Weekly Intakes – PTWIs) and Acceptable Daily Intakes (ADIs) as guidelines for food additives and certain contaminants in foods, the USFDA recommends Reference Daily Intake (RDI) values for some essential elements from foods, the UK/European Union has adopted Tolerable Daily Intake (TDI) to estimate the amount of a substance that can be ingested over a lifetime without appreciable health risk [Ikem and Egiebor (2005)]. These safety guidelines represent an intake where there is essentially no risk, as far as it can be judged from the available scientific evidence [Ikem and Egiebor (2005), UKFSA (1999), Joint FAO/WHO Expert Committee (2004)].

One of the most important objectives of a food surveillance and regulation programme is to obtain some basic information on the chemical composition of foods as there are good epidemiological evidences that the diet is one of the important factors which predispose individuals to chronic diseases. Furthermore, such information would go a long way in assisting in the monitoring and surveillance programme of foods, as well as to undertake risk assessment.

2.6 Permissible Limits

Continuous ingestion of diets that are deficient, unbalanced or extensively high in a particular trace element invariably induces changes in the functioning forms, activities and concentrations of the elements in the body tissues or fluids so that they fall below, or rise above the permissible levels [Sigel (1980)]

Independent of the source, the determination of these metals is of paramount importance to help assess the quality and purity of foods. Most countries and some International Organisations have established regulatory guidelines for the maximal metal concentrations allowed in foods [Tahan *et al* (1995)].

The recommendations by some International organizations are as tabulated in Table 2.4

Table 2.4: Recommendations by International Organisations for some Elements

Element	FAO	WHO	Joint FAO/WHO
As	0.5	-	15 (inorganic)
Cd	0.5	-	7
Cu	30	30	3.5
Fe	-	-	5.6
Hg	-	-	5
Pb	0.5	2.0	25
Sn	-	250	14
Zn	40	-	7

[Adeniyi *et al* (2008), Ikem and Egiebor (2005), Joint FAO/WHO Expert Committee (2004), Tuzen (2003), UKFSA (1998 and 1999), Abou-Arab *et al* (1996), CAOBISCO (1996)].

The European dietary limits are: Hg: 0.5,Pb: 0.1, Cd: 0.1, Sn: 200 all in mg/Kg [EC Commission regulation No. 1881 (2006)].

The maximum permissible limits in μg/g for some metals fixed by some countries are tabulated below in Table 2.5.

Table 2.5: Maximum Permissible Limits set by some Countries for some Elements

Country	Al	As	Cd	Cr	Cu	Hg	Ni	Pb	Sn	Zn
Australia	-	1	-	-	-	-	-	-	250	-
Brazil	-	-	1.0	0.1	-	-	-	-	250	-
Hong Kong	-	6	-	-	-	-	-	-	-	-
Japan	-	-	-	-	-	0.3	-	-	-	-
Libya	-	-	-	-	50	-	-	6	-	300
Malaysia	-	1	-	-	-	-	-	-	-	-
New Zealand	-	2	-	-	-	-	-	-	-	-
Poland	-	-	-	-	-	-	-	-	100	-
Singapore	-	1	-	-	-	-	-	-	-	-
UK	10	1	0.1	-	-	0.5	-	1	200	-
USA	-	-	0.2	8.0	120	0.5	1	1 ,4	-	-

[Ashraf (2006), NZFSA (2006), Ikem and Egiebor (2005), Joint FAO/WHO Expert Committee (2004), UKFSA (1998 and 1999), Tarley *et al* (2001), Tahan *et al* (1995), Sarmani *et al* (1993)].

Generally, most of the results obtained by various researchers as reviewed above are within the ranges specified by most countries and International Organisations.

2.7 Analytical Techniques

Several techniques have been used for the detection and determination of levels of trace elements in foods. These include: Electroanalytical, Nuclear magnetic resonance, Atomic absorption spectrometry, Inductively coupled plasma–Optical emission spectrometry, Direct mercury analysis, X–Ray fluorescence spectrometry; Neutron activation analysis, Inductively coupled plasma–Mass spectrometry, Particle induced X–Ray emission, Rutherford backscattering spectrometry.

The choice of an analytical method for an exercise of this nature depends on whether few (one or two) elements or multi–elements determination are required, concentration range to be investigated, accuracy required, availability of equipment, cost and time. Consequently, X–Ray fluorescence (XRF) spectrometry has been chosen for this Research work, having met most of the above conditions.

Cost not withstanding, its multi-elemental determination ability, non–destructiveness, excellent precision, accuracy, sensitivity, possible sub–ppm level of detection, and availability amongst others, informed its choice for this work. It also has the advantage of minimal sample preparation which thus eliminates loses of the material and/or addition of unwanted material to the components of the sample.

2.8 X–Ray Fluorescence (XRF) Spectrometry

X–Ray fluorescence (XRF) spectrometry provides one of the simplest, most accurate and most economical analytical technique for the qualitative and quantitative

determination of the chemical composition of a wide variety of matrices at major, minor or trace levels of abundance. It is universally recognised as a non–destructive method for rapid and sequential, or simultaneous analysis of elemental composition of a material. XRF is reliable and requires no, or very little, sample preparation [Margui *et al* (2005), Hamilton (1979), SPECTRO (2005), UOI (2002)]

XRF spectrometer is made up of the following components: A source of excitation consisting of a high energy X-ray tube, an optical system for selecting X-rays frequencies and a detector which integrates X-ray intensity or counts X-ray photons integrating or counting circuits for measurements.

Depending on the application, X–ray fluorescence can be produced by using not only X-rays, but also other primary excitation sources like alpha particles, protons or high energy electron beams [AMPTEK (2002)]. The X–ray region of the electromagnetic spectrum lies between 0.1 and 100Å.

XRF has the advantage of being non–destructive, multi–elemental, fast and cost–effective. Furthermore, it provides a fairly uniform detection limit across a large portion of the elements on the Periodic Table and is applicable to a wide range of concentrations. Its main disadvantage is that analyses are generally restricted to elements heavier than fluorine. In other words, it can be used for a wide range of elements, from sodium (11) to uranium (92), and provides detection limits at the sub-ppm level; it can also measure concentrations of up to 100% easily and simultaneously [SPECTRO (2005)].

2.8.1 General principles of XRF spectrometry

In XRF measurement, the sample is subjected to an excitation that displaces an electron from one of the inner shells of the atom [Gouldon (1978)].

An inner shell electron is excited by an incident photon in the X-ray region. During the de-excitation process, an electron is moving from a higher energy level to fill the vacancy. The energy difference between the two shells appears as an X-ray, emitted by the atom. The X-ray spectrum acquired during the above process reveals a number of characteristic peaks. The energy of the peaks leads to the identification of the elements present in the sample (qualitative analysis) and the peak intensity provides the relevant or absolute elemental concentration (semi-quantitative or quantitative analysis) [UOI (2002)].

Hence, since each element has electrons with more or less unique energy levels, the wavelength of light emitted is characteristic of the element. And the intensity of light emitted is proportional to the elements concentration.

2.8.2 Types of XRF spectrometer

There are generally two types of XRF spectrometers: wavelength dispersive (WD-XRF) and energy dispersive (ED-XRF). Wavelength dispersive system uses a diffraction crystal to focus specific wavelengths onto a detector. A wavelength range is scanned by changing the angle in which the X-rays strike the crystal. An energy dispersive spectrometer focuses all the emitted X-rays onto an energy analysing detector [Gouldon (1978)].

The XRF spectrometer used for this study is the EDXRF. Model SL 12170 with Si(Li) detector. It is owned by and located at Centre for Energy Research and

Training/Ahmadu Bello University (CERT/ABU). The sources used for this work are the Cd-109 and Fe- 55.

Other sources that are commonly used are: Co-57 and Am-241. These sources emit X-rays of definite energy, therefore being capable of efficiently exciting a limited number of atoms [UOI (2002)].

Chapter 3: MATERIALS AND METHODS

3.1 Materials

3.1.1 Samples

The samples analysed in this study were two (2) brands of canned sardine fish (*Titus™ and Princesse* ™) and four (4) brands of canned tomato paste (*De Rica* ™, *La Bianca* ™ *Pomo* ™ and *Tomato-Fun* ™).

The sample sizes were determined using the student *t*–test at 95% level of confidence.

3.1.1.1 Canned sardine fish

Eleven samples each of the two brands (making a total of twenty – two) were purchased and coded as follows (for identification purposes) in addition to their Batch Numbers and Best Before Dates as shown in Tables 3.1 and 3.2 below:

Table 3.1: Particulars of *Titus*™ Sardine Fish

Identification Code	Batch Number	Best Before (B.B) Date
SF 101	IC 342P	08/12/11
SF 102	IC 342P	08/12/11
SF 103	IC 342P	08/12/11
SF 104	IC 342P	08/12/11
SF 105	IC 342P	08/12/11
SF 106	IC 348P	14/12/11
SF 107	IC 348P	14/12/11
SF 108	IC 348P	14/12/11
SF 109	IC 348P	14/12/11
SF 110	IC 348P	14/12/11
SF 111	IC 348P	14/12/11

Table 3.2: Particulars of *Princesse*™ Sardine Fish

Identification Code	Batch Number	Best Before(B.B) Date
SF 201	AK 02C	31/12/11
SF 202	AK 02C	31/12/11
SF 203	AK 02C	31/12/11
SF 204	AK 02C	31/12/11
SF 205	AK 02C	31/12/11
SF 206	AK 02C	31/12/11
SF 207	AK 365P	31/12/11
SF 208	AK 365P	31/12/11
SF 209	AK 365P	31/12/11
SF 210	AK 365P	31/12/11
SF 211	AK 365P	31/12/11

**Production dates were not provided on the containers on the two sardine fish brands*.

As at the time of procurement of these samples up to the stage of analysis, there was no sardine fish canning factory in Nigeria.

3.1.1.2 Canned tomato pastes

Similarly, eleven samples each of the four brands (making forty-four in all) were purchased and given identification codes in addition to their Batch Numbers and Best Before Dates as shown in Tables 3.3 to 3.6 below:

Table 3.3: Particulars of *De Rica*™ Tomato Paste

Identification Code	Batch Number	Manufacture Date	Best Before (B.B) Date
TP 101	C 278	N.S*	Oct., 2009
TP 102	C 278	"	Oct., 2009
TP 103	C 278	"	Oct., 2009
TP 104	C 278	"	Oct., 2009
TP 105	C 278	"	Oct., 2009
TP 106	C 313	"	Nov., 2009
TP 107	C 313	"	Nov., 2009
TP 108	C 313	"	Nov., 2009
TP 109	C 313	"	Nov., 2009
TP 110	C 313	"	Nov., 2009
TP 111	C 313	"	Nov., 2009

N.S. = Not stated

Table 3.4: Particulars of *La Bianca* ™ Tomato Paste

Identification Code	Batch Number	Manufacture Date	Best Before(B.B) Date
TP 201	B 129	May, 2007	May, 2009
TP 202	B 129	May, 2007	May, 2009
TP 203	B 129	May, 2007	May, 2009
TP 204	B 129	May, 2007	May, 2009
TP 205	B 164	June, 2007	June, 2009
TP 206	B 164	June, 2007	June, 2009
TP 207	B 164	June, 2007	June, 2009
TP 208	B 164	June, 2007	June, 2009
TP 209	B 164	June, 2007	June, 2009
TP 210	B 164	June, 2007	June, 2009
TP 211	B 164	June, 2007	June, 2009

Table 3.5: Particulars of *Pomo* ™ Tomato Paste

Identification Code	Batch Number	Manufacture Date	Best Before (B.B) Date
TP 301	P 137/I	May, 2007	May, 2009
TP 302	P 137/I	May, 2007	May, 2009
TP 303	P 137/I	May, 2007	May, 2009
TP 304	P 137/I	May, 2007	May, 2009
TP 305	P 137/I	May, 2007	May, 2009
TP 306	P 137/I	May, 2007	May, 2009
TP 307	P 137/I	May, 2007	May, 2009
TP 308	P 206/T	July, 2007	July, 2009
TP 309	P 206/T	July, 2007	July, 2009
TP 310	P 206/T	July, 2007	July, 2009
TP 311	P 206/T	July, 2007	July, 2009

Table 3.6: Particulars of *Tomato-Fun* ™ Tomato Paste

Identification Code	Batch Number	Manufacture Date	Best Before (B.B) Date
TP 401	TM 012	July, 2008	July, 2010
TP 402	TM 012	July, 2008	July, 2010
TP 403	TM 012	July, 2008	July, 2010
TP 404	TM 012	July, 2008	July, 2010
TP 405	TM 012	July, 2008	July, 2010
TP 406	TM 012	July, 2008	July, 2010
TP 407	TM 012	July, 2008	July, 2010
TP 408	TM 012	July, 2008	July, 2010
TP 409	TM 012	July, 2008	July, 2010
TP 410	TM 012	July, 2008	July, 2010
TP 411	TM 012	July, 2008	July, 2010

3.1.2 Sample Composition

Composition of the samples as indicated on the containers are as tabulated in Tables 3.7 and 3.8 below:

Table 3.7: Composition of the Canned Sardine Fish Samples

Brand	Composition
(i) Titus (SF 101-111)	Fish, vegetable oil and salt (% not stated)
(ii) Princesse (SF 201-211)	Fish (75%), vegetable oil and salt (% not stated)

Table 3.8: Composition of the Canned Tomato Paste Samples

Brand	Composition
(i) De Rica (TP 101 – 111)	28% paste and Salt
(ii) La Bianca (TP 201 – 211)	28% (min) paste and Salt
(iii) Pomo (TP 301 – 311)	22% (min) paste and Salt
(iii) Tomato-Fun (TP 401 – 411)	28 - 30% (min) paste and Salt

3.1.3 Sampling points

The samples that were used for this work were procured from three markets each in two cities, Kaduna and Zaria, in Kaduna State of Nigeria. The samples of both products obtained from each of the towns are as outlined in Table 3.9.

Table 3.9: Points of Purchase of the Samples

Town	Market(s)	Samples	
		Sardine Fish	**Tomato Pastes**
Kaduna	Abubakar Gumi Central Market, Kasuwar Barchi, Ungwan Sanusi Market.	SF 101 – 105 SF 201 – 206	TP 106 – 111 TP 201 – 204 TP 301 – 307 TP 401 – 406
Zaria	Sabon Gari Market, Tudun Wada Market, ABU Main Campus Markets.	SF 106 – 111 SF 207 – 211	TP 101 – 105 TP 205 – 211 TP 308 – 311 TP 407 – 411

Both sardine fish samples (*Titus* and *Princesse*) are of Morroccan origin; *De Rica* tomato paste is from Italy, both *La Bianca* and *Pomo* tomato pastes are produced in Ghana while *Tomato-Fun* tomato paste is produced in Nigeria.

Figures 2 and 3 below are respectively the maps of Africa showing Nigeria and that of Nigeria showing the location of the two cities (Kaduna and Zaria) where the samples were procured.

Figure 2: Map of Africa showing Nigeria – the Country where the Samples were Procured

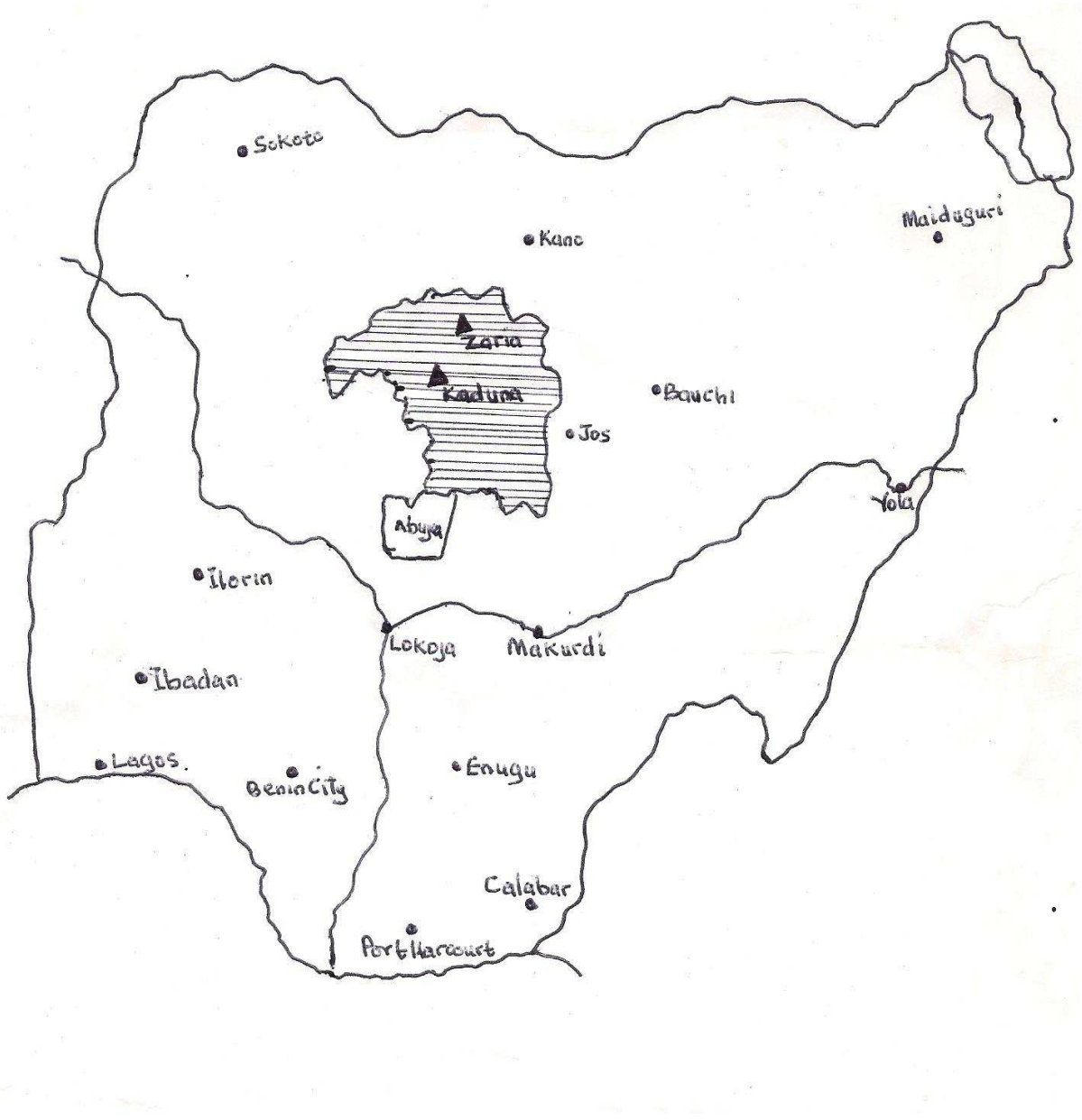


Figure 2: Map of Nigeria showing the Two Cities where the Samples were Procured

Key: *Kaduna and Zaria (where the Samples were Procured)*
Kaduna State of Nigeria

3.2 Instruments/Apparatus

1 The XRF spectrometer used for this study is the EDXRF. Model SL 12170 with Si (Li) detector. The sources used for the work are the Cadmium–109 (Cd–109) and Iron–55 (Fe–55).

2. Memmart Oven: Schutzart Din 40050 IP 20. Type UM200: For drying the samples.

3. Agate Mortar and Pestle: For grinding.

4. Hydraulic press: For pressing the samples into pellets.

5. Mettler Precision Balance (Model H_6 dig cap 160g), 4dp.

All are available at CERT/ABU, Zaria

3.3 Chemicals

Organic Liquid Binder: A mixture of Toluene and PVC.

3.4 Analytical Procedure for XRF

The procedure adopted for preparing and analysing the samples as well as sensitivity calibration is the method used by the CERT/ABU, Zaria, (2008) and are as outlined below:

3.4.1 Sample Preparation

The samples with the same batch were opened, made into composite and dried in a Memmart Oven, Type UM200, for about six (6) hours at about 100^{o}C. The dried samples were than ground with an agate mortar and pestle to grain size of 125µm.

Pellets of 19mm diameter of the ground samples were prepared from about 0.3–0.5g of the samples earlier mixed with 3 drops of an organic liquid binder (made from

Toluene and PVC). The pellets were then pressed with an hydraulic press with a weight of 10,000kg (10 tonnes). At this stage the samples are ready for the analysis.

3.4.2 Sample Analysis

The samples were analysed using EDXRF spectrometer, Model SL 12170 with Si(Li) detector. Measurements were performed using an annular 25mCi ^{109}Cd as the excitation source, that emits Ag – K X-rays (22.1KeV) in which case all elements with lower characteristic excitation energies were accessible for the detection in the samples. Furthermore, this system consists of a Si(Li) detected with a resolution of 170eV for the 5.90 KeV line, coupled to a computer controlled ADC card.

Modified version of Emission-Transmission (E–T) method was used for the quantitative analysis of the samples. This involves the use of pure target material (Mo) to measure the absorption factors in the sample. The Mo target serves as a source of monochromatic X–rays which are excited through the sample by primary radiation and then penetrate the sample on the way to the detector. In this way, the absorption factor is experimentally determined which the programme uses in the quantification of the concentration of the elements. In addition, the contribution to the Mo–K peak intensity by the Zr–K is subtracted for each sample.

3.4.3 Calibration

Sensitivity calibration of the system was performed using thick pure metal foils (Ti, Fe, Co, Ni, Cu, Zn, Zr, Nb, Mo, Sn, Ta, Pb) and stable chemical compounds (K_2CO_3, $CaCO_3$, Ce_2O_3, WO_3, ThO_2, U_3O_8). The spectra of the samples were collected for 3000 seconds with the ^{109}Cd source and 2000seconds for the ^{55}Fe source and the spectra were then evaluated using the AXIL–QXAS program.

Chapter 4: RESULTS AND DISCUSSION

The results obtained for the analyses of the samples using the X–Ray Fluorescence technique (XRF) as well as the observations on them are as outlined below.

4.1 Canned Sardine Fish Samples

Tables 4.1 and 4.2 show the concentrations in mg/kg (ppm) of each of the elements detected in the two brands of the canned sardine fish samples (*Titus*^{TM} and *Princesse*^{TM}) analysed.

Table 4.1: Concentration Levels of Trace Elements Detected in *Titus*^{TM} Sardine Fish (SF 101 – 111) (in mg/kg)

Batch Numbers (With ID. Code)	Br	Cu	Fe	Nb	Ni	Zn
IC 342P (SF 101 to 105)	*N.D.*	222	641	*N.D.*	254	176
IC 348P (SF 106 to 111)	72	204	595	28	*N.D.*	133

N.D.: Not Detected

Table 4.1 above shows the concentration levels of trace elements in the two batches of *Titus* sardine fish. A total of six trace elements, bromine, copper, iron, nobium, nickel and zinc were detected in the samples of this sardine fish brand. Generally, the samples with the batch coded SF 101 to 105 gave higher values than those with code SF 106 to 111.

While both batches contain copper, iron and zinc, bromine and nobium were not detected in the batch with code SF 101 to 105. In the same vein, nickel was not found in the batch with code SF 106 to 111.

Compared to results obtained in similar studies (Table 4.3) and the maximum limits recommended by some Countries and International Organizations (Table 4.4), the values obtained in this study for this brand (*Titus*) of sardine are significantly higher.

Table 4.2: Concentration Levels of Trace Elements Detected in *Princesse*^{TM} Sardine Fish (SF 201 – 211) (in mg/kg)

Batch Numbers (With ID. Code)	Br	Cu	Fe	Zn	Zr
AK 02C (SF 201 to 206)	58	167	*N.D.*	*N.D.*	*N.D.*
AK 365P (SF 207 to 211)	*N.D.*	*N.D.*	995	160	39.7

N.D.:Not Detected

Table 4.2 above shows the concentration levels of trace elements in the two batches of *Princesse* sardine fish samples. A total of five trace elements, bromine, copper, iron, zinc and zirconium were detected in the samples of this sardine fish brand.

However, none of the two batches contain the same set of elements. That is, the batch with the code SF 201 to 206 showed the presence of bromine and copper only, while the batch with the code SF 207 to 211 has iron, zinc and zirconium.

All the values obtained for the elements in this brand of the sardine fish and for which limits have been fixed are above results obtained in similar works (Table 4.3) and the recommended maximum limits set by most Countries and International Organisations (Table 4.4).

Table 4.3: Comparison with Values Obtained in some Related Studies on Canned Sardine Fish (in mg/kg)

Trace Element	This Study	1*	2*	3*
Copper	222	1.75	1.30	1.6
Iron	995	29.20	–	159
Nickel	254	<0.02	–	–
Zinc	176	20.62	3.48	21

***N.B.**

1. *Ikem and Egiebor (2005) in USA;*
2. *Abou – Arab et al (1996) in Egypt;*
3. *Tahan et al (1995) in Venezuela.*

Table 4.4: Comparison with Maximum Limits set by FAO, WHO, Joint FAO/WHO and some Countries (in mg/kg)

Trace Element	This Study	FAO	WHO	Joint FAO/WHO	Countries
Bromine	72	*N.F.*	*N.F.*	*N.F.*	*N.F.*
Copper	222	30	30	3.5	50[a]; 120[b]
Iron	995	*N.F.*	*N.F.*	5.6	*N.F.*
Nickel	254	*N.F.*	*N.F.*	*N.F.*	1[b]
Nobium	28	*N.F.*	*N.F.*	*N.F.*	*N.F.*
Zinc	176	*N.F.*	*N.F.*	7	300[a]
Zirconium	39.7	*N.F.*	*N.F.*	*N.F.*	*N.F.*

N.F.: Not Found

a: Libya
b: USA

The two batches of the samples SF101 to 111 (*Titus* sardine) (Table 4.1) do not contain zirconium found in the *Princesse* sardine. Also the two batches of SF 201 to 211 (*Princesse* sardine) (Table 4.2) contain neither nobium nor nickel detected in *Titus* sardine.

Across the brands, the highest values of bromine, copper and zinc were found in *Titus* sardine while *Princesse* sardine presented the highest values for iron.

These variations in the elements detected and their respective concentrations may not be unconnected with the duration of exposure to contamination in water, feeding habit of the fish, concentrations of contaminants in the water column, water chemistry, uptake and elimination rates, contamination of fish during handling and processing, quality of canned fish, shelf life of the canned fish amongst other possible reasons [Ikem and Egiebor (2005), Abou-Arab *et al* (1996), Tahan *et al* (1995)].

The following chart (Figure 4) shows the distribution of the elements detected in the two brands of the sardine fish. It compares the amount of each of the elements detected, indicating which of the brands is richer and in what element.

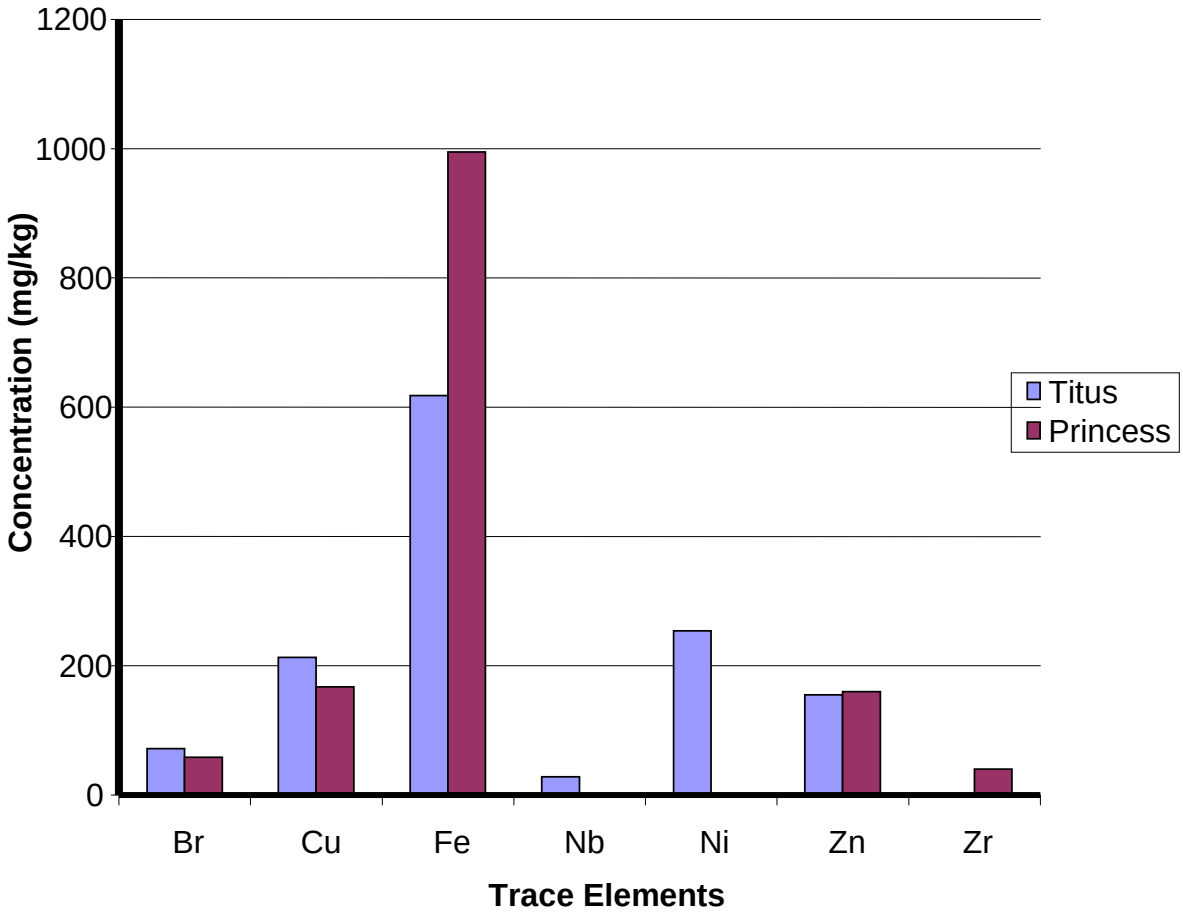


Figure 4: Trace Elements Distribution Chart for the Two Brands of Canned Sardine Fish

The Figure 4 above further indicates that these products are packed full of essential trace elements (copper, iron, nickel and zinc). Their consumption should however continued to be watched since at high concentrations they can result in adverse health effects [Tuzen (2003), Cid *et al,* (2001), Pickford (1981), CAOBISCO (1996)].

Arsenic, cadmium, chromium, lead and mercury which are generally known to affect health adversely even at low concentrations [Ikem and Egiebor (2005), Kocak *et al* (2005), Cubadda *et al* (2003, Jarup (2003), Ryan *et al* (2001), Hills (1997), Abou-Arab *et al* (1996), Burgess (1996), Lindsay (1981), Pickford (1981), Hamilton (1979), Prasad (1978), Florkin and Stortz (1971), ATSDR (2006), CAOBISCO (1996), CEH (2008), CPUT (2005), NZFSA (2006), OSHA (2006), UKFSA (1998 and 1999), USFDA (2008), health.enotes.com (2007)] were not detected in the two brands of the sardine fish (*Titus* and *Princesse*) studied.

4.2 Canned Tomato Paste Samples

Tables 4.5 to 4.8 show the concentrations in mg/kg (ppm) of each of the elements detected in the four brands of tomato paste (*De Rica, La Bianca, Pomo* and *Tomato–Fun*) samples analysed.

Table 4.5: Concentration Levels of Trace Elements Detected in *De Rica*^{TM} Tomato Paste (TP 101 – 111) (in mg/kg)

Batch Numbers (With ID. Code)	As	Br	Cu	Fe	Pb	Ti
C 278 (TP 101 to 105)	*N.D.*	107	*N.D.*	1,390	1,250	5,740
C 313 (TP 106 to 111)	167	*N.D.*	354	1,260	*N.D.*	*N.D.*

N.D.: Not Detected

The table above (Table 4.5) shows the presence of six trace elements and their respective concentrations in *De Rica* tomato paste samples. These are arsenic, bromine, copper, iron, lead and titanium. Of these, four were found in the batch with code TP 101 to 105 of this brand of tomato paste (*De Rica*) viz: bromine, iron, lead and titanium. The batch with code TP 106 to 111 on the other hand contains arsenic, copper and iron.

The only element that is common to both batches of this brand of tomato paste (*De Rica*) that were analysed is iron.

Of serious concern is the presence of arsenic with a value of 167mg/kg in the batch with code TP 106 to 111 and lead with a value as high as 1,250mg/kg in the batch with code TP 101 to 105 which are far higher than any tolerable limit.

The values in mg/kg obtained in similar work done on canned tomato pastes for some of the trace elements detected as well as the maximum limits recommended by International Organisations and some Countries are as tabulated in Tables 4.9 and 4.10 respectively.

Table 4.6: Concentration Levels of Trace Elements Detected in *La Bianca*^{TM} Tomato Paste (TP 201 – 211) (in mg/kg)

Batch Numbers (With ID. Code)	Br	Fe	Zr
B 129 (201 to 204)	*N.D.*	2,850	*N.D.*
B 164 (205 to 211)	112	1,250	59.3

N.D.: Not Detected

Only three elements were detected in the two batches of this tomato paste brand (*La Bianca*) as recorded in Table 4.6 above. These are: bromine, iron and zirconium. The batch with range TP 205 to 211 is the one that has the three elements. The batch with the range TP 201 to 204 indicated the presence of only iron.

As in the *De Rica* tomato paste (Table 4.5), iron is the only element that is common to both batches. Arsenic and lead, however were not detected in any of the batches of the *La Bianca* tomato paste brand.

The values in mg/kg obtained in similar work done on canned tomato pastes for some of the trace elements detected as well as the maximum limits recommended by International Organisations and some Countries are as tabulated in Tables 4.9 and 4.10 respectively.

Table 4.7: Concentration Levels of Trace Elements Detected in *Pomo*^{TM} Tomato Paste (TP 301 – 311) (in mg/kg)

Batch Numbers (With ID. Code)	Cr	Fe	Pb	V
P 137 I (TP 301 to 307)	1,930	2,330	289	3,610
P 206 T (TP 308 to 311)	*N.D.*	1,260	*N.D.*	*N.D.*

N.D.: Not Detected

For *Pomo* tomato paste, the elements found in the samples analysed and their concentrations are as shown in Table 4.7 above.

Four elements were detected in the two batches of this brand (*Pomo*), namely: chromium, iron, lead and vanadium. Like with *De Rica* and *La Bianca* tomato paste samples (Tables 4.5 and 4.6 respectively above, iron is the only element that is common to both batches of this *Pomo* tomato paste brand.

The batch with code TP 301 to 307 showed the presence of all the four elements including lead and chromium (which are elements of health concern) with values of 289mg/kg and 1,930mg/kg respectively. The batch with code TP 308 to 311 indicated the presence of only Iron.

Arsenic detected in *De Rica* tomato paste (Table 4.5) was not detected in the samples of this brand (*Pomo*) analysed.

All the values obtained are above the maximum limits that have been set by Countries and International Organisations as compared in Table 4.10.

Tomato–Fun, the tomato paste processed in Nigeria revealed the presence of the trace elements and concentrations tabulated in Table 4.8 below:

Table 4.8: Concentration Levels of Trace Elements Detected in *Tomato-Fun*™ Tomato Paste (TP 401 – 411) (in mg/kg)

Batch Numbers (With ID. Code)	Cr	V
TM 012 (TP 401 to 411)	1,800	3,080

Only two elements were detected in this batch of the *Tomato-Fun* tomato paste brand analysed. These are chromium with a value of 1,800mg/kg and vanadium with a value of 3,080mg/kg.

Arsenic and lead which are among the other elements of health concern and detected in *De Rica* (both arsenic and lead) and *Pomo* (lead only) were not detected in samples of this brand (*Tomato-Fun*).

The values in mg/kg obtained in similar work done on canned tomato pastes for some of the elements detected in the four brands of the tomato pastes in this study (*De Rica*, *La Bianca*, *Pomo* and *Tomato-Fun*) as well as with the maximum recommendations for elements for which limits have been fixed by some Countries and International Organisations are compared in Tables 4.9 and 4.10 below:

Table 4.9: Comparison with Values Obtained in some Related Studies on Canned Tomato Pastes (in mg/kg)

Trace Element	This Study	1*	2*
Copper	354	1.968	7.3
Iron	2,850	–	7.8
Lead	1,250	0.372	–

***N.B.**

**1. Kocak et al (2005) in Turkey;*
**2. Turker and Yuksel (1997) in Turkey;*

Table 4.10: Comparison with Maximum Limits set by FAO, WHO, Joint FAO/WHO and some Countries (in mg/kg)

Trace Element	This Study	FAO	WHO	Joint FAO/WHO	Countries
Arsenic	167	0.5	*N.F.*	15 (inorganic)	1[a,b,c,d], 2[e], 6[f]
Bromine	112	*N.F.*	*N.F.*	*N.F.*	*N.F.*
Chromium	1,930	*N.F.*	*N.F.*	*N.F.*	0.1[g], 8[**h**]
Copper	354	30	30	3.5	50[**j**]; 120[**h**]
Iron	2,850	*N.F.*	*N.F.*	5.6	*N.F.*
Lead	1,250	0.5	2.0	25	0.1[k], 1[**d**], 4[h], 6[**j**]
Titanium	5,740	*N.F.*	*N.F.*	*N.F.*	*N.F.*
Vanadium	3,610	*N.F.*	*N.F.*	*N.F.*	*N.F.*
Zirconium	59.3	*N.F.*	*N.F.*	*N.F.*	*N.F.*

N.F.: Not Found

a: Australia
b: Malaysia
c: Singapore
d: UK
e: New Zealand
f: Hong Kong
g: Brazil
h: USA
j: Libya
k: European Communities

All the values as outlined in both tables 4.9 and 4.10 above can be seen to be comparatively far lower than the values obtained in this research work.

The following Figure (Figure 5) shows the distribution of the elements detected in the four brands of the tomato pastes. It can be seen in this chart that tomato pastes contain a very large proportion of iron. The presence of lead, chromium and arsenic in very high amounts needs to be given serious attention.

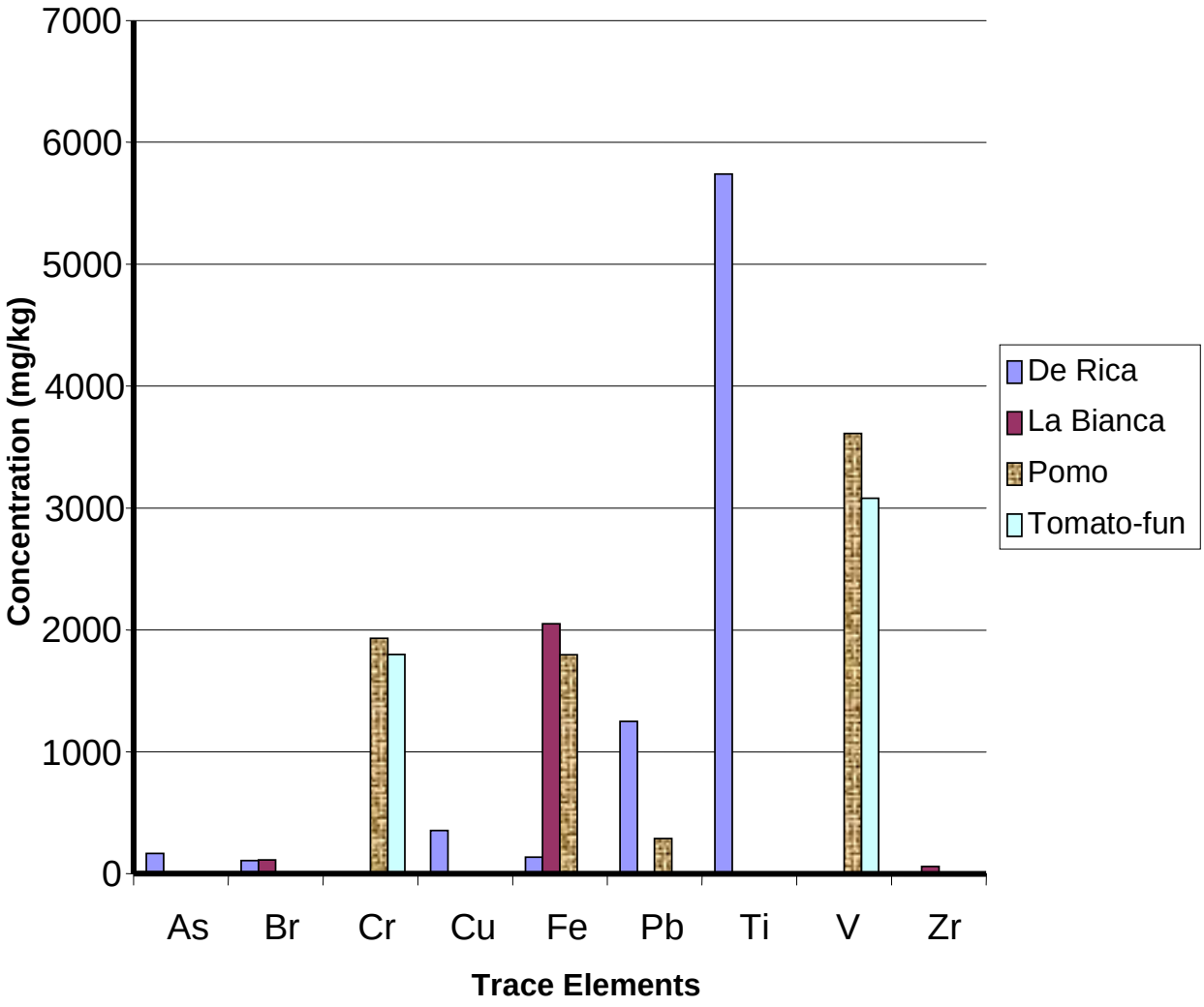


Figure 5: Trace Elements Distribution Chart for the Four Brands of Canned Tomato Pastes

Across the four brands of the tomato pastes (*De Rica*, *La Bianca*, *Pomo* and *Tomato-Fun*), arsenic, copper and titanium were found in *De Rica* only; bromine is common to only *De Rica* and *La Bianca* with *La Bianca* giving the higher value of 112mg/kg; chromium and vanadium were detected in *Pomo* and *Tomato–Fun* only, with *Pomo* indicating the higher value for both elements (1,930mgCr/kg and 3,610mgV/kg); Only *Pomo*, surprisingly, did not indicate the presence of iron – its highest value of 2,850mg/kg being shown by *La Bianca*; lead was detected in *De Rica* and *Pomo* with *De Rica* giving the higher value of 1,250mg/kg; zirconium was found in only *La Bianca* with a concentration level of 59.3mg/kg.

These variations may have arisen from the source of supply of the raw tomatoes which is a consequence of the environment of cultivation, concentration of contaminants in the environment, variety of tomatoes, means of pest control, type of plant nutrients that may have been applied, contamination during handling and processing and quality of lacquer coating of the cans amongst other possible causes.

Although the values of the concentration levels of the elements in this study are very high especially for the elements of very serious health concern like arsenic, chromium and lead detected in this research. They are the total elemental concentrations.

As far as this research has indicated however, these trace elements are present in the samples analysed and the values for the elements for which limits have been set are higher than the maximum tolerable limits set by some Countries and International Organisations as can be seen in Table 4.10.

4.3 The Trace Elements Detected and Health Implications

The concentration levels of the trace elements detected in this study compared to the limits set by Countries and International Organisations as well as their possible implications on human health are outlined below.

Arsenic (As)

Arsenic was found in only *De Rica* tomato paste with a concentration of 167mg/kg. This value is higher than the maximum limit set by FAO (0.5mg/kg) and countries with regulations on arsenic (e.g. Auistralia: 1, Hong Kong: 6, Malaysia: 1, New Zealand: 2, Singapore: 1 and UK: 1 all in mg/kg). This is also higher than the limit of 0.015mg/kg for inorganic arsenic set by Joint FAO/WHO Expert Committee on Food Additives and Contaminants.

Its effects on health include human cancer, anaemia, liver damage, cardiac abnormalities, dermatitis, decreased nerve conduction velocity. Acute exposure can cause lung distress and death, cardiac arrhythmia and other adverse side effects. [Jarup (2003), CEH (2008), CPUT (2005), NZFSA (2006), OSHA (2006), USFDA (2008), health.enotes.com (2007)].

Bromine (Br)

Bromine was found in both brands of Sardine fish (*Titus* and *Princesse*) and two brands of tomato paste (*De Rica* and *La Bianca*). The highest value in the sardines was in *Titus* (72mg/kg) while for Tomato pastes, it was in *La Bianca* (112mg/kg). No recommendation on maximum limit was found for this element in the literature.

The effects of bromine on health are that it is corrosive to human tissues. It can cause sore throat, cough, chest tightness, bronchospasm, pulmonary oedema,

drooling, difficulty swallowing with retrosternal and abdominal pain and circulatory collapse. Severe cases may be complicated with haematemesis and shock. The larynx may be burned causing air way obstruction and difficulty clearing bronchial secretions. Bromine also causes damage to organs like liver, kidneys, lungs, milt and the nervous system [HPA (2008), LENNTECH (2008)]..

Chromium (Cr)

Chromium was detected in *Pomo* and *Tomato-Fun* but not in other tomato paste brands and sardine fish samples. The highest value (1,930mg/kg) was obtained in *Pomo*. This value is also far above the maximum limits of 0.1mg/kg and 8.0mg/kg set by Brazil and USA respectively.

Chromium(III) is an essential nutrient to humans helping the body to use sugar, protein and lipids. It is an integral part of “Glucose Tolerance Factor” (GTF) – maintaining normal glucose tolerance in organisms. Excessive amount of chromium(III) however may cause adverse health effects. The chromium(VI) is more toxic to humans and is a known carcinogen [Ikem and Egiebor (2005), Cubadda *et al* (2003), Ryan *et al* (2001), Prasad (1978), ATSDR (2006)]..

Copper (Cu)

Copper was detected in both brands of sardine fish (*Titus* and *Princesse*) and *De Rica* tomato paste. The highest value in the sardines (222mg/kg) was found in *Titus*. A value of 354mg/kg was found in *De Rica* tomato paste. All the values are higher than the 30mg/kg recommended by FAO and WHO, Libya (50mg/kg) and USA (120mg/kg) that have set limits for this element.

Copper plays an essential role in collagen synthesis and good health but very high intake of it can cause nausea, diarrhoea, stomach cramp, kidney damage and Wilson's disease. Deficiency leads to anaemia, hyperlipidemia. Unexcreted excess may be found deposited in the eyes [Dudek (2006), Abou-Arab *et al* (1996), Prasad (1978), Williams (1971), ATSDR (2006), NZFSA (2006), health.enotes.com (2007)]..

Iron (Fe)

With the exception of *Tomato–Fun*, all the brands of tomato pastes and both brands of the sardine fish showed the presence of iron with *La Bianca* giving the highest value of 2,850mg/kg in the case of tomato pastes and *Princesse* (995mg/kg) in the case of sardine fish samples. In all the cases, the values are higher than the maximum recommendation of 5.6mg/kg by the Joint FAO/WHO Expert Committee on Food Additives and Contaminants.

The effects of iron on health are that: its deficiency causes anaemia, impaired immune function, fatigue, intolerance to cold temperature while excess of it gives rise to a condition of siderosis. Other toxic effects include joint disease, enlarged liver amenorrhoea, impotence, etc. [Dudek (2006), Ikem and Egiebor (2005), Williams (1971), OSHA (2006), health.enotes.com (2007)].

Lead (Pb)

This element which is one of the most hazardous elements to human beings was detected in *De Rica* (1,250mg/lkg) and *Pomo* (289mg/kg). In both cases, the values are higher than the maximum limits set by all Countries and Organisations with regulation for Lead such as UK (1mg/kg), Libya (6mg/kg), European Communities (0.1mg/kg), WHO (2.0mg/kg), FAO (0.5mg/kg) and the Joint FAO/WHO Expert Committee on Food Additives and Contaminants (0.025mg.kg).

Lead is a typical cumulative poison. It is known to induce reduced cognitive development and intellectual performance in children; and increased blood pressure and cardiovascular disease in adults. Lead toxicity may cause anaemia, anorexia, brain damage, abdominal pain, convulsions, hypertension, miscarriage, tremours, renal tube nephrosis and diminished IQ (Intelligence Quotient) in children. It also damages the kidney and the reproductive system, and is responsible for encephalopathies in the central nervous system [Kocak *et al* (2005), Jarup (2003), CAOBISCO (1996), CEH (2008), NZFSA (2006), UKFSA (1998 and 1999), health.enotes.com (2007)]..

Nickel (Ni)

This trace element was detected in only *Titus* sardine fish with a value of 254mg/kg. This value is higher than the USA recommendation of 1mg/kg.

The effects on health of nickel include: Deficiency of it leads to diminished growth and impaired normal iron absorption leading to anaemia. Nickel has been associated with allergies. It is carcinogenic and can cause respiratory problems. Ingestion of toxic levels can result in headache, vomiting, vertigo and nausea [Kirchgessner (1978), ATSDR (2006), CAOBISCO (1996), CEH (2008), health.enotes.com (2007)].

Nobium (Nb)

Nobium was detected in only *Titus* sardine fish with a value of 28mg/kg. No recommendation on permissible limit was found in the literature for this trace element.

Nobium causes eye and skin irritation. It is retained primarily in the lungs and secondarily in the bones. It interferes with calcium as an activator of enzyme systems [LENNTECH (2008)].

Titanium (Ti)

This trace element was detected only in *De Rica* tomato paste with a very high level of 5,740mg/kg. No recommendation on permissible limits was found in the literature for titanium.

Titanium has low toxicity. However, dust inhalation or excessive exposure to it may cause tightness and pain in the chest, coughing and difficulty in breathing. Contact with skin and eye may cause irritation [LENNTECH (2008)].

Vanadium (V)

Vanadium was detected in *Pomo* and *Tomato–Fun* Tomato pastes, both giving significantly high values of 3,610mg/kg and 3,080mg/kg respectively. No recommendation on permissible limits was found for vanadium in the literature.

The effects of vanadium on health Include: High uptake of vanadium can cause bronchitis, pneumonia, irritation (of lungs, eyes, throat and nasal cavities), cardiac and vascular diseases, inflammation of stomach and intestines, damage to the nervous system, bleeding of liver and kidneys, skin rashes, severe trembling and paralysis, etc. [LENNTECH (2008)].

Zinc (Zn)

Only the sardine fish brands (*Titus* and *Princesse*) showed the presence of zinc. The observed maximum value of 176mg/kg was found in the *Titus*. This is above the limit of 7mg/kg and 40mg/kg, set by Joint FAO/WHO Expert Committee on Food

Additives and Contaminants, and FAO respectively, but lower than the 300mg/kg set by Libya.

Zinc plays some role in growth and development, deoxyribonucleic acid (DNA) synthesis, acrodermatitis enteropathica theraphy. Its deficiency may lead to growth retardation, mental lethargy, delayed wound healing, delayed sexual maturation, and impotence, anorexia, taste abnormality, alopecia, dermatitis, hypogonadism, enlarged liver, decreased immune function, etc. Toxic effects of zinc include: anaemia, diarrhoea, fever, renal failure, reproductive failure, nephritis, extensive lesions in the kidney [Dudek (2006), Abou-Arab *et al* (1996), Kirchgessner (1978), Prasad (1978), Halsted *et al* (1972), health.enotes.com (2007)].

Zirconium (Zr)

Zirconium was detected in one sardine fish brand (*Princesse*) and one tomato paste brand (*La Bianca*). No recommendation on permissible limits was found in the literature for Zirconium.

Zirconium has low systemic toxicity, however at high concentrations, there is risk of cancer [LENNTECH (2008)].

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The values of the concentration levels obtained can be said to be at least indicative of the presence of these trace elements in these products. Therefore these products need to be closely and continuously monitored in order to ensure safety of the consuming populace.

4.4 The Results and the Set Objectives

From the results obtained and the information gathered from the various literature cited, the objectives of the research can be said to have been achieved as follows:

1. The samples analysed indeed contain trace elements, some of which (like arsenic, chromium and lead) are not only known to be toxic but indicated very high level of concentrations that can affect human health adversely.
2. Even the trace elements that are considered essential for healthy living (like copper, iron, nickel and zinc) are present and have shown very high concentrations in the samples analysed. It is known that at elevated amounts (more than normal required by the body), they negatively affect our health. Therefore, their consumption need to be seriously monitored.
3. There is a need to introduce regulations for elements for which limits are yet to be fixed or made available such as titanium and vanadium which this study showed to have extremely high level of concentration in the canned tomato pastes (5,740mg/kg and 3,610mg/kg respectively). Similarly concern about bromine (as bromate) has of recent been raised and this element was detected in this study in both the sardine fish and the tomato paste samples. All these three elements (bromine, titanium and vanadium) impact negatively on health. As such there is a need to introduce more stringent regulations with respect to the primary and secondary sources of these elements.
4. In line with the observations made, the level of safety of these products (canned sardine fish and canned tomato pastes) can be said to be still low, despite the presence of some nutritive essential elements (which this study has indicated to be on the very high side), since the danger posed by the presence of potentially

toxic elements far outweighs whatever benefit these products might contribute. Moreover there can be less dangerous sources of the essential elements.

Chapter 5: SUMMARY, CONCLUSION AND RECOMMENDATION

5.1 Summary

The presence of trace elements, mostly trace metals in foods have become a matter of serious concern in view of their now known potential health effects even at sub-ppm level for some of them like mercury, lead, cadmium, chromium and arsenic. Even those considered essential for healthy living often impact on health negatively at high concentrations.

The level of concentrations of trace elements in samples of two brands canned sardine fish (*Titus* and *Princesse*) and four brands of tomato pastes (*De Rica, La Bianca, Pomo* and *Tomato-Fun*) was determined with X–Ray Fluorescence spectrometer. The results obtained indicated generally very high values for all the elements detected in all the samples analysed.

There is therefore the need for continuous monitoring of all foods, especially when canned (since canned foods can add more elements and/or increase their levels in the foods) in order to assess their level of safety.

5.2 Conclusion

The samples obtained and analysed all indicated the presence of varying types of trace elements. In all, seven elements were detected in the two brands of the sardine fish samples (bromine, copper, iron, nobium, nickel, zinc and zirconium) and nine in the four brands of the tomato paste samples (arsenic, bromine, chromium, copper, iron, lead, titanium, vanadium and zirconium).

In the sardine fish samples analysed, only copper, iron, nickel and zinc can be said to be essential for human health. However at deficient or elevated levels they can be harmful. Their levels of concentration in this study were seen to be high. Bromine, nobium and zirconium are not known to have any beneficial effect. In fact, they are harmful and can be very dangerous to humans.

In the tomato paste samples analysed, copper and iron detected in them are the only elements that benefit humans; arsenic, lead and chromium which are elements of serious health concern were observed to be present in very large amounts far above any national or international recommendation; bromine, titanium vanadium and zirconium which have various forms of potential health implications were also detected in the tomato paste samples analysed.

In this study, the generally very hazardous elements were found in the tomato pastes and as such require caution in their consumption.

5.3 Recommendations

Following the outcome of this study, the recommendations below are being put forward for possible action:

1. All canned sardine fish and tomato pastes should be thoroughly screened to determine if any toxic elements and even those safe at low concentrations but potentially toxic at high concentrations are present and at what level of concentration. This action is recommended to be applied to all canned foods, especially the imported ones.
2. All producers/importers of these products should be mandated to make available verifiable analytical reports on every batch of these products to relevant regulatory

agencies who shall in turn carry out follow up tests before authorising their release for public consumption.

3. Further work is suggested to be carried out on the specific form or state of the elements since it is not all the oxidation states or forms of some of the elements that are toxic.
4. Consumption of these products should be monitored so that the level of intake of the essential nutritive elements among them remain within the beneficial level in the body and the effects of the toxic ones get equally reduced.
5. Thorough screening of especially all the tomato pastes imported into or produced in Nigeria should be given high priority as this study has shown that lead, arsenic and chromium were detected in only the tomato paste samples.

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