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ASSESMENT OF HEAVY METALS INTRODUCED INTO FOOD THROUGH MILLING PROCESS:

HEALTH IMPLICATIONS

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PRINCE JAMES ADETI

(10443752)

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DECLARATION

I Prince James Adeti hereby declare that, with the exception of references to other people's work which have been duly acknowledged, this work is the result of my own research undertaken under the supervision of Rev (Dr) S. Akoto Bamford and Dr. Francis G. Ofosu. It has not been presented for any other degree in this university or elsewhere either in part or in whole

…… ……

PRINCE JAMES ADETI DATE

(STUDENT)

…….. ……

REV (DR) S. AKOTO BAMFORD DATE

(PRINCIPAL SUPERVISOR)

……. ……

DR. FRANCIS G. OFOSU DATE

(CO-SUPPERVISOR)

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DEDICATION

This work is dedicated to Almighty God, the giver of life and provider of wisdom. My Sister Juliana Baby Adeti, for her invaluable piece of advice and prayers for me throughout my life. It is also dedicated to my lovely Wife, Henrietta Abla Nyablordzro, for her understanding, prayers and care for me throughout this work. May the almighty God bless us all.

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ABSTRACT

The present study was conducted to characterised and assess heavy metal contamination in food through milling process and their health implications. Grinding plate made from Ghana, India and Nigeria purchased from the Ghanaian open market were used for this work. Maize from the same farm was milled into flour using the three grinding plates inserted into three different corn milling machines operating on commercial bases. The first grinding was done immediately after the insertion of the newly sharpened plates into the machines. The plates were left for continuous daily usage. Subsequent milling of the maize was done after intervals of one month. The grinding plates and maize flour was analysed using Atomic absorption spectrophotometer (AAS). The results recorded indicated that the heavy metals content of the Ghanaian, Indian and Nigerian made plates had the similar metal contents but varied in terms of the individual metal concentrations. Flour from the Ghanaian made plates had the highest level of contaminants with the least from that of the Indian made plates. Generally the highest levels of contamination were observed in the first milling for the three plates as compared to the three subsequent milling at monthly intervals. The contamination levels showed a decreasing trend from the first month (first milling) to the fourth month (fourth milling). Cu, Cr and Ni showed concentrations above the permissible limit set by FAO/WHO in milled maize using Ghanaian made plate. Copper (Cu) recorded a concentration value between 15.04 mg/kg to 10.21mg/kg, 11.25 mg/kg to 9.13mg/kg and 10.36mg/kg to 9.68mg/kg using the Ghanaian-, Indian and Nigerian made plate respectively. Chromium (Cr) recorded a concentration between 1.51 mg/kg to 0.96 mg/kg, 1.03 mg/kg to 0.91 mg/kg and 0.98mg/kg to 0.80 mg/kg using Ghanaian-, Indian and Nigerian made plates

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respectively. Nickel (Ni) recorded a concentration value between 23.23 mg/kg to 10.43 mg/kg, 11.46 mg/kg to 10.43 mg/kg and 12.55 mg/kg to 10.09 mg/kg Using Ghanaian-, Indian and Nigerian made plates respectively. Which shows that the Cu, Cr and Ni concentration decreases from the first month (first milling) to the fourth month (fourth milling).The Ghanaian made plate was found to wear faster relative to Nigerian- and Indian made plate with that of showing the least rate of wear.

The Ghanaian made plates was found to cause more contamination than the other two but generally, the Indian made plates caused least contamination. The Indian made plates had the least Cd and Pb concentration levels. The elemental concentration and the risk assessment calculations have shown that contamination of milled products are highest within the first month of the use of the grinding plates but can decreases considerably with time.

The HRI value for first milled maize with locally made grinding plate showed human health problem for Cr and Ni metals contaminations in the maize flour.

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CHAPTER ONE

INTRODUCTION

Food grinding machine (Corn-mill) is a unit operation designed to break solid materials into smaller pieces, usually pulverized into fine powder. It is a machine used to process cereals, legume, nuts and spices into flour. It is an indispensable tool in the flour industry. It can be found in cities, towns and villages across the Ghana due to the dependence on cereal food product by the country folks. It has a pair of circular grinding plates which is made of cast iron (Kwofie et al, 2006). Cast iron is made by re-melting pig iron, often along with substantial quantities of scrap iron, scrap steel, lime stone, carbon and taking various steps to remove undesirable contaminants. Cast iron is normally used for machinery parts to resist wear and tear. Iron is alloyed with nickel, chromium, copper, molybdenum and silicon to increase the tensile strength (Johnson, 1977). Both surfaces of the plates have small ridges running from edge to centre. Grinding is done by rotating one mobile plate against a stationary plate. In the process, grains that pass between the plates are crushed to powder.

These grinding plates produced from the casting method are not regulated by any standard procedure for defects (standard chemical composition) and health impacts before being introduced to the market, hence may pose high risk to end users. Although wearing of these plates into the food during the milling process is inevitable, the rate of these wear and the levels of contamination they introduce into our food is not known. A defective plate (in chemical structure) will wear faster. The health impacts of using a defective grinding plate are enormous.

The use of food grinding machine is a common practice in food preparation and processing in Ghana and many other developing nations. These grinding plate,

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invariably, contain varying amounts of elements that regulate many vital biological processes.

A heavy metal is any metal or metalloid with a potential negative health effect. In very small amounts (at approved concentrations), many of these metals are necessary to support life. These elements include vanadium, manganese, iron, cobalt, copper, zinc, selenium, strontium and molybdenum. The determination of trace elements particularly heavy metals such as arsenic, mercury, chromium, iron, lead, cadmium, cobalt, copper, manganese, nickel, zinc, etc. has received increasing attention in food chemistry, nutrition, and pollution studies. However, in larger amounts, they may cause acute, severe or chronic toxicity (Afal & Wiener, 2014). They may build up in biological systems and pose significant health hazards. Some may, not be needed at all for body processes and functioning (Bronstein et al, 2011).

Some metal which are known to be toxic are not required by the body in any amount (ATSDR, 2011). Heavy metals with adverse health effects in human metabolism (including lead, cadmium, and mercury) present obvious concerns due to their persistence in the environment.(ATSDR, 2000; ATSDR, 2004; ATSDR, 2007a; ATSDR, 2007b; ATSDR, 2008a; ATSDR, 2008b; ATSDR, 2011).

Acute heavy metal intoxications may damage central nervous function, the cardiovascular and gastrointestinal systems, lungs, kidneys, liver, endocrine glands, and bones (Adal et al, 2013). Chronic heavy metal exposure has been implicated in several degenerative diseases of these same systems and may increase the risk of some cancers (Wu et al, 2012).

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Processing of food for consumption is as vital and important as the food itself. During this processing such as milling with machine and pounding with wooden pestle and mortar, toxic materials or elements from the processing implements may be introduced into the matrix of the food material.

The grinding plates that can be found on the Ghanaian market are mostly the locally manufactured plate. Nigerian and Indian made ones which are the only foreign made available. The foreign made ones have brand names such as radget, amuda, rex, premier, bin, England and bamford. The higher the quality of the grinding plates the longer it takes to wear out and the safer it is because there would be less worn out metals in the corn flour. The plate type and the method of grinding can affect the degree of contamination in the resulting flour. The analysis of grinding plate is necessary to determine the heavy metal composition to ascertain the quality, mostly in relation to the toxic metal contents.

1.2 Problem Statement

The use of food grinding machine is a common practice in food preparation and processing in Ghana and many other developing nations. Wearing of this grinding plate into the food during the milling process is inevitable. The grinding plates are locally produced or imported. In the Ghanaian market, some are from India and Nigeria but most of the Corn-mill grinding plates are locally produced and they are not regulated by any standard quality before being introduced to the market, therefore the possibility of posing high risk to the end users of the milling products. The bad quality ones wear at faster rates introducing more toxic elements into the milled products. In addition, very little study has been done to characterised heavy metals in

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grinding plates and the level of contamination of milled food products hence the needs for research in this area.

1.3MainObjective

To assess the extent to which grinding plates introduce heavy/toxic metals into food that goes through milling process.

1.3.1 Specific objectives:

a) Elemental characterisation of local and foreign grinding plates in the Ghanaian market that are used for milling.

b) To assess wearing effect of the grinding plate during the milling process.

c) To evaluate the health risk implications on the consumers of milled products

1.4 Relevance and Justification

Maize is a staple food in Ghana and is grown in many parts of the tropics for both human and animal consumption. Maize is processed into corn flour which is used in the preparation of many local foods such as Akple", "Banku","kenkey","apreprensa" "abolo" "tuo zaafi" and maize porridge (Lokko et al, 2004).

Work has been done on the milled maize but not much has been done to ascertain the quality of the grinding plate, especially the locally manufactured ones. With special regards to the grinding plate contaminating milled products with heavy metals namely arsenic Cadmium (Cd), copper (Cu), iron (Fe), lead (Pb) and zinc (Zn).Cadmium and

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lead are toxic metals and non-essential to the human body. They are not required by the body in any amount (ATSDR, 2011). Ingestion of these metals can have adverse health effects in human metabolism leading to serious health consequences (ATSDR, 2000; ATSDR, 2004; ATSDR, 2007a; ATSDR, 2007b; ATSDR, 2008a; ATSDR, 2008b; ATSDR, 2011). It is imperative that their concentration in the grinding plate and the milled food is known and the health implications evaluated

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CHAPTER TWO
LITERATURE REVIEW

2.1 Food Milling

Food is any substance consumed to provide nutritional support for the body. It is usually of plant or animal origin, and contains essential nutrients, such as fats, proteins, vitamins, or minerals (Aquilera et al, 1999). The substance is ingested by an organism and assimilated by the organism's cells to provide energy, maintain life, or stimulate growth.

The earliest records of food production in Africa show that indigenous crops have long been milled to produce coarse flour for cooking (Basey, 2004). Traditional crops such as yam, sorghum, millet and teff have been ground for centuries either with a crude mortar and pestle fashioned from a tree stump and branch or by using flat stones or rubbing stones. All these types of grinding systems are still in common use throughout Africa today. Newer crops, such as rice, maize and cassava, have been introduced in more recent centuries, and new milling techniques have followed.

In the mid-nineteenth century, electric motors were invented and high speed machines, such as hammer and plate mills, began to replace traditional stone mills. As electricity became available in many parts of Africa, motor-driven Traditional rubbing and hand mills gained its importance. However, it was grinding stones until the introduction of the diesel engine in the early twentieth century that high- speed mills were seen in more significant numbers across the continent. A relatively low-speed, water-cooled diesel engine can, for example, power a hammer mill, producing maize flour of acceptable quality. These mills are in widespread use in rural parts of the world in areas where no electricity grid is available. Diesel-powered grain mills are limited to areas with access to fuel and spare parts.

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Many people still cannot afford paying for commercial grain-milling services and they grind by hand using traditional techniques. Therefore, pounding is a common sight and sound in many areas. It is often a social activity, carried out predominantly by women, and many hours are spent each day in this laborious and time-consuming task. The pestle may weigh up to 4 kg, and pounding requires a lot of effort. The stone mill or quern, either hand-, animal- or motor-driven, is relatively unknown in Africa despite having given good service in many other countries. This machine operates on the same principle as plate mills but uses large stones instead of plates and is set with a vertical axis. The skills of dressing stones have not been acquired in areas where appropriate stones have not been easily available.

2.1.1 Objectives of milling

The main objective of milling is to improve the digestibility of the grain for human or animal consumption. A typical grain is surrounded by a hard coat or husk, which protects the germ and the endosperm, the energy-rich starchy centre of the grain. The layer between the husk and the endosperm is called bran. The awn is the spiked part at the end of the grain. The aim of milling for human consumption is to produce a palatable meal or flour and to expose the starch in the endosperm to the digestion juices of the stomach. The objective is not to produce a very fine flour or paste but rather to mill the grain to a point of coarseness that is acceptable to the consumer.

The main purpose of milling animal feed is to prevent the grain passing straight through the animal without being fully digested. There is little to be gained from

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producing very fine flour from a digestive point of view. Very dusty animal feed can also cause respiratory problems when fed dry.

Preferences for different types of milled products vary throughout Africa with respect to the fineness of final product. Many people in East Africa prefer a very fine flour to make “nzima” or “ugali”, a smooth gruel, while other people in Central and West Africa prefer coarser, unshelled flour, which gives more texture to the product (Jone, 2010).

2.2 Principles of milling

Mechanism of fracture of a grain

Grain subjected to a force responds in three distinct stages. The first stage is called elastic deformation, the second is termed plastic deformation, and the final stage is termed breakage or fracture. Elastic deformation means that the grain deforms under force but returns to its original shape when the force is removed. As the force is increased on a grain, plastic or permanent deformation takes place, even when the force is removed. The grain appears to be flattened or distorted in some way but is still in separate, identifiable units. The grain eventually fractures when forces are increased further.

The chief mechanisms of fracture in milling are compression and shear. Other effects occur, such as cutting, sawing, tearing and abrasion, but they are only a combination of shear and compression. A dry grain shatters in a random matter when compression and shear is applied. The grain then breaks into coarse chunks, some fine particles and very fine dust. Dry grains do not deform when grinding forces are applied, but they produce cracks that eventually lead to grain failure. On the other hand, moist grains

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produce a range of closer-sized particles as well as fewer and finer particles when forces are applied. Through compression, they can be formed into flat discs that are ideal for a wide range of meals for human and animal consumption. Shearing of moister grain tends to tear the grain along defined plains of failure.

The stages of compression and machines between two flat plates, or between a flat plate and a bed of grain. In some mills, the grain is suspended in the air where it is struck by a high-speed plate or hammer. A larger grain has more inertia and, therefore, fractures more easily. As the grain become finer, it has less inertia and force causes some plastic deformation before the grain fractures or breaks. This is caused by the propagation of cracks from the points of stress, which are normally the points of contact. On the other hand, a moist grain is relatively soft and deforms to some extent elastically when pressure is applied. As the force on the grain is increased, a moist grain is capable of retaining more plastic deformation than a dry grain before it breaks (FAO, 2001).

2.3 Different types of small milling machine

2.3.1 Hammer mills

Hammer mills are very common throughout Africa. As the name implies, hammers in the mill grind grains through impact. The grains are placed into a holding hopper on top of the hammer mill, and a small control gate allows the grains to trickle into the grinding chamber. The grains feed into the path of the hammers either through the centre of the front plate or through the top side of the case. The hammers strike the grains and shatter them before they can pass through the screen surrounding the hammers. The flour produced either falls by gravity into a chamber or sack below, or

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is propelled by air flow up through a cyclone into a holding container. The airflow is provided by either the fan effect of the hammers or by extra fan blades mounted on the hammer shaft. A hammer mill consists of a large cylinder with a horizontal shaft that drives a rotor with several rows of free-swinging hammers.

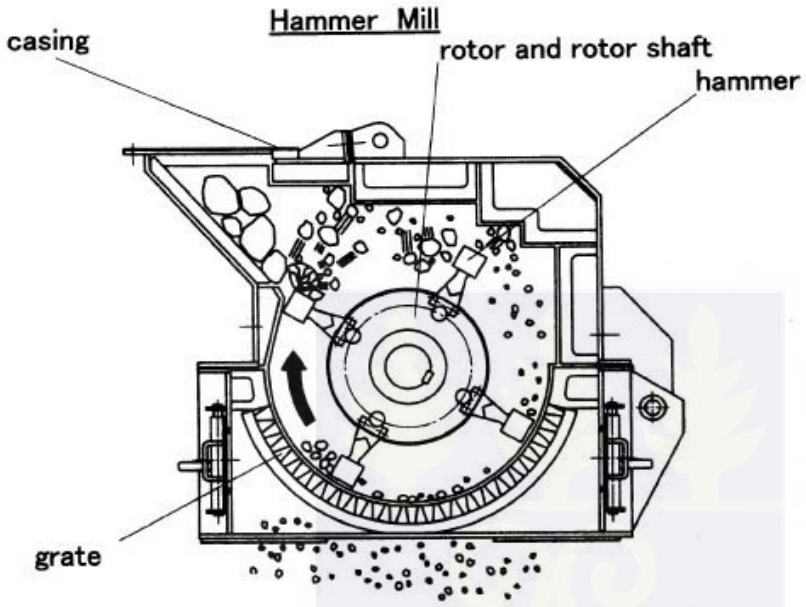

Figure 2.1 Hammer mill

The hammers rotate inside a perforated metal screen through which the flour is drawn. The hammers are driven by two or four sets of V-section belts between the engine and the mill. The hammers spin at high speed, usually between 2000 and 4 000 revolutions per minute to achieve a hammer-tip speed of about 60 m/second. The speed of the mill has to be matched to the size of the mill as a small mill needs to run at higher revolutions than does a larger mill. Some hammer mills have screens that cover the mill around 360 degrees. More popular designs have screens around 180 degrees of the lower periphery as this allows easily made replacement screens to be used. Beater bars are often incorporated into the upper semi- circle against which the grain impacts.

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Screens are made by perforating blank sheets of steel. This is not commonly practised in Africa, and screens have to be imported. Screen replacement represents one of the main running costs of the mill. The rate of screen replacement depends on thickness of the steel. As a rough guide, it is possible to punch a hole through steel of the same thickness as the diameter of the hole. For example, a screen for a hammer mill with 0.5 mm holes would be made from 0.5 mm thick steel. The larger the hole size, and hence the thicker the steel, the longer the screen will last.

There are also simple hammer mills that have no transmission belts and are driven directly by the motor. The base plate of the motor is fixed to the mill chamber, and an accurate alignment of the mill is essential. Mills without transmission belts are well suited for local manufacture. Simple hammer mills can have a small electric engine, but they also work well in petrol and diesel-driven mills.

Hammer mills work well for grains with a minimum moisture content of 12 percent. Drier crops are very dusty when ground and can create health problems for mill operators. However, the drier the crop, the less power is needed for milling. As a rule of thumb, five percent less power is needed for every one percent reduction in moisture content. In most African climates, grain can be sun-dried to have a moisture content of 12 percent or less in dry regions (May, 1986).

2.3.2 Plate mills

Plate mills are popular in West Africa and the Sudan and operate with a greater component of shear than compression. A plate mill consists of a circular chamber made of cast iron or steel within which two plates with a narrow gap between them are mounted face to face. The plates are grooved in order to provide a shear mechanism.

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Figure 2.2 Plate mill

When grains are introduced into the centre of the mill, the plates shear the grains between them. One of the plates rotates and the grains revolve, working their way to the outer edge of the plate before dropping by gravity into a holding sack below.

The grains lodge in the rotating plate and are sheared by the grooves in the opposing plate. As the grains move to the edges of the plates, the grooves become shallower and reduce the size of the grains. The design of grooves follows a very old style developed for stone mills several thousand years ago.

Plates are usually about 200–300 mm in diameter. Plates are normally aligned in a vertical direction, but horizontal alignment is more convenient when the mill is run by a diesel engine. Plate mills can run as fast as possible but normally at about 2 500–3 500 revolutions/minute, as overheating of the plates limits the speed of the mill.

Frictional heating imposes power limits. For example, a plate mill with 300 mm plates cannot be driven by an engine with more than 12 kW. However, the speed of mill is not a critical factor to the mechanism of grinding. Plate mills operate more effectively with soft and moist grains that shear easily than with hard and brittle grains. It is common in West Africa to add water at the time of grinding. The milled product has

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to be used very quickly in order to prevent fermentation. The fineness of the flour ground is adjusted by increasing the pressure on the grain by narrowing the gap between the plates. This is done with a simple hand wheel connected to the outer plate by a shaft. The mill should not be run empty because grains in the mill are needed in order to lubricate the action and, thus, prevent wear. Excessive wear is caused when the plates come into contact with each other. A fine flour or meal from a plate mill is obtained by re-circulating the product in the mill for a second or third grind. When the plates wear out, they have to be replaced with new ones. Cast-iron or steel plates are preferable but old mills can also be refurbished by replacing worn plates with locally made steel plates. Grooves are cut with the help of simple grinding wheels. Such replacement plates provide a short-term emergency solution for grinding cereals and they can be used for softer fruits and vegetables.

2.4 Comparison of milling machines

2.4.1 Product considerations

A new mill should make a similar product to that made by traditional milling techniques. Traditional crops and cooking methods are deeply entrenched in most societies, and there is little desire for initiating change.

A hammer mill grinds anything brittle including straw, mineral ores and dried roots. Any produce to be ground should flow easily when milled. Very soft produce reduces the throughput of a mill and tends to block up the screens so that the mill eventually ceases to function. On the other hand, plate mills are a little more versatile. Any fresh or partially dried fruit or vegetables may be ground in plate mills, provided that the

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product responds to gravity. Plate mills can operate at a lower speed than a hammer mill and can be turned by hand (where small enough), by animals, wind, water or any other variable speed source. The material to be milled may be soft or hard. Water may be added to cereals but the product must then be processed quickly in order to prevent fermentation.

2.4.2 Technical considerations

Hammer mills have a power requirement that ranges between two and 50 kW, while motor-driven plate mills generally demand less power and 0.5–12 kW is sufficient. As a rule of thumb, about 1 kW can mill 25–30 kg of produce per hour

Machines and spares for hammer mills are often made locally at lower prices than imported parts. Some components, such as screens, are rarely made locally and need to be imported, especially those of a very fine size.

Plate mills of 0.5 kW are usually made for grinding soft fruits and vegetables, and the plates can be made from locally produced steel. Plate mills are not popular for grain milling as they have to be manufactured from chilled cast iron, which is rarely available in Africa.

2.5 Heavy Metal

The term “heavy metal” assumes a variety of different meanings throughout the different branches of science. Although “heavy metal” lacks a consistent definition in medical and scientific literature, the term is commonly used to describe the group of dense metals or their related compounds, usually associated with environmental pollution or toxicity (Duffus, 2002). Elements fitting this description include lead,

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mercury, and cadmium. The rather broad definition of heavy metals may also be applied to toxic metalloids (a chemical element that has properties that include a mixture of those of metals and non-metals), like arsenic, as well as nutritionally-essential trace minerals with potential toxicities at elevated intake or exposure (eg, iron, zinc, or copper) (Duffusl, 2002; Bronstein et al, 2011).

Although "heavy metal" toxicities due to lead, mercury, and cadmium are generally considered rare in mainstream medicine, less well-recognized is that chronic accumulation that may not achieve classical acute toxicity thresholds may nevertheless contribute to adverse health effects.

Regarding acute toxicity, according to the 2011 National Poison Data System annual report, there were 7337 *reported* unintentional heavy metal exposures in the United States, resulting in 26 serious health outcomes and 2 deaths (Bronstein et al, 2011). While data from the National Health and Nutrition Examination Survey (NHANES) shows a decade of encouraging year-over-year decreases in acutely toxic heavy metal exposure in the United States, there are still a significant number of people with blood levels that may put them at risk for chronic accumulation, and therefore toxicity, over time (CDC, 2013a). For example, in the United States, children are exposed to lead in at least 4 million households. Children are particularly sensitive to lead intoxication, both acute and chronic, and there is no identified safe level of lead exposure in children (CDC, 2013b; Koller et al, 2004; Handler et al, 2012; CDC, 2012). Further, pregnant women risk toxic exposure to the developing fetus since the mobilization of stored lead from the mother's bones can leach into the bloodstream, and this is more likely the result of chronic rather than acute lead exposure in the mother (Miranda et al, 2010). With several toxic metals lacking robust pathways for elimination or

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otherwise remaining in the body for a long time, body burdens of some toxic metals (eg, lead, mercury, cadmium) may increase with age (Bjermo et al, 2013).

While a specific toxic metal has the potential to exert detrimental effects by select mechanisms, there are several common features among toxic heavy metals. One of the most widely studied mechanisms of action for toxic metals is oxidative damage due to direct generation of free radical species and depletion of antioxidant reserves (Ercal et al, 2001). Mercury, cadmium, and lead, for example, can effectively inhibit cellular glutathione peroxidase, reducing the effectiveness of this antioxidant defence system for detoxification (Reddy et al, 1981). Many toxic heavy metals act as molecular "mimics" of nutritionally essential trace elements; as a result, they may compete with essential metallic cofactors for entry into cells and incorporation into enzymes (Jang et al, 2011). For example, cadmium can compete with and displace zinc from proteins and enzymes; lead is chemically similar to calcium; and thallium is a potassium mimic in nerves and the cardiovascular system (Buchko et al, 2000; Jang et al, 2011; Thévenod et al, 2013).

2.6 Development of Heavy Metal Toxicity

The severity and health outcomes of toxic heavy metal exposure depend on several factors, including the type and form of the element, route of exposure (oral/inhalation/topical/ocular), duration of exposure (acute vs. chronic), and a person's individual susceptibility (CDC, 2012).

Acute toxicities arise from sudden exposures to substantial quantities of some metals (such as from occupational exposure to aluminium dust or breaking a mercury-containing thermometer) and typically affect multiple organ systems, commonly the gastro intestinal (GI) tract, cardiovascular system, nervous system, endocrine system,

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kidneys, hair, and nails (Jang et al, 2011). Acute exposures to some metals (mercury, gold, nickel, and others) can also cause hypersensitivity (allergic) reactions (Sinicropi et al, 2010).

Chronic toxicities are manifested as conditions that develop over extended periods from chronic exposure to relatively low concentrations (eg, sustained environmental exposure). Symptoms of chronic heavy metal toxicity (described later in this protocol) can be similar to other health conditions and may not be immediately recognized as intoxications. Increased cancer risk is a common feature of chronic exposure to certain metals; the exact mechanism of their carcinogenicity is not completely understood, although many are weak mutagens (cause DNA damage), can disrupt gene expression, and deregulate cell growth and development (Galanis et al, 2009). They can also interfere with innate DNA repair systems (Koedrith et al, 2011). In addition, certain metals may affect gene expression and alter gene function (Arita et al, 2009; Martinez-Zamudio et al, 2011).

The International Agency for Research on Cancer (IARC) has classified several metals based on their potential carcinogenicity to humans. Group 1 metals include arsenic and arsenic compounds, cadmium, gallium, and nickel compounds. Group 2B (possible carcinogens) include cobalt and cobalt compounds (Sinicropi et al, 2010; Galanis et al, 2009).

2.7 Common Heavy Metal Toxicants and Associated Health Risks

2.7.1 Mercury

Mercury has no known beneficial role in human metabolism, and its ability to affect the distribution and retention of other heavy metals makes it one of the most

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dangerous toxic metals (Houston, 2011). Mercury toxicity can arise from ingestion of metallic mercury or mercury salts (which are generally poorly bioavailable) or by inhalation of mercury vapour (which is readily absorbed) (ATSDR, 2001). The relatively high solubility and stability of certain mercury salts in water enables them to be readily taken up and bio transformed to methyl mercury by certain fish. These forms are readily absorbed through the gastrointestinal tract and are becoming a major source of mercury exposure in humans (Houston, 2011). Dimethyl mercury, a mercury compound chemically synthesized in the laboratory, can also be absorbed through the skin, and several cases of fatal exposure among laboratory workers have been reported (Nierenberg et al, 1998; Bernhoft, 2012).

Although humans can excrete small amounts of mercury in urine or faeces as well as via exhalation or sweating, they lack an active robust mechanism for mercury excretion, allowing levels to accumulate with chronic exposure (Houston, 2011; Sällsten et al, 2000; Houston, 2011). Mercury, particularly when inhaled as mercury vapours, can distribute to many organs, but may concentrate in the brain and kidneys (ATSDR, 2001). It can also cross the placenta and be found in breast milk (Yang et al, 1997).

Mercury exerts its toxic effects by competing with and displacing iron and copper from the active site of enzymes involved in energy production; this induces mitochondrial dysfunction and oxidative damage (Houston, 2011). Mercury can also directly accelerate the oxidative destruction of cell membranes and LDL cholesterol particles as well as bind to and inactivate the cellular antioxidants N-acetyl cysteine, alpha-lipoic acid, and glutathione (Houston, 2011). Because of its effect on cellular defence and energy generation, mercury can cause widespread toxicity and symptoms

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in several organ systems: nervous system (eg, personality changes, tremors, memory deficits, loss of coordination); cardiovascular system (eg, increased risk of arterial obstruction, hypertension, stroke, atherosclerosis, heart attacks, and increased inflammation); gastrointestinal tract (eg, nausea, diarrhoea, ulceration); and kidneys (failure) (Houston, 2011; ATSDR, 2001). Mercury may also accumulate in the thyroid and increase the risk of autoimmune disorders (Gallagher et al, 2012), and may cause contact dermatitis (Caravati et al, 2008).

2.7.2 Lead

Lead toxicity is one of the most frequently reported unintentional toxic heavy metal exposures and the leading cause of single metal toxicity in children (Bronstein et al, 2011). Lead has no known beneficial function in human metabolism. Human environmental exposure is often through lead-containing paint, food stored in lead can liners, food stored in ceramic jars, or contaminated water (pipes cast in lead or soldered using lead solder). Inhalation of lead particulates is a primary route of occupational lead exposure, while oral ingestion is a primary form of exposure in the general population (ATSDR, 2008a; Rodrigues et al, 2010). Animal models also suggest that lead can be absorbed through the skin; lead acetate can be found in some cosmetic products (ATSDR, 2008a; ATSDR, 2007b). Children absorb lead up to 8-times more efficiently than adults (Abelsohn et al, 2010). Ingestion of deteriorating lead-based paint chips or dust is the primary source of lead exposure in children (CDC, 2009; Manton et al, 2000). Also, toys and other children's products may contain lead or be painted with lead-based paint; imported children's products pose greater risk (Rossiter, 2013; EPA, 2013; Lipton et al, 2007; DOH, 2007). In 2009 and 2011, the Consumer Product Safety Commission began requiring lower lead levels in children's products (as of 2011, allowing less than 100 ppm (parts per million) of lead

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in accessible parts of children's products with some exceptions) (CPSC, 2013); however, caution is still warranted. Because it mimics calcium, most absorbed lead is stored in the bones of children and adults where it can remain for decades. Conditions that cause release of calcium from the bones (fracture, pregnancy, age-related bone loss) will also release stored lead from bones, thus allowing it to enter into the blood and other organs. Lead can leave the body through feces or urine (ATSDR, 2007b).

In addition to disrupting calcium metabolism, lead can mimic and displace magnesium and iron from certain enzymes that construct the building blocks of DNA (nucleotides) and disrupt the activity of zinc in the synthesis of heme (the carrier of oxygen in red blood cells) (Kirberger et al, 2013). Chronic, low-level lead exposure (blood levels <10 µg/dL) is associated with increases in hypertension risk and reduction in kidney function. Higher levels of lead exposure affect the endocrine glands (changing the levels of thyroid hormones [at serum lead levels over 40-60 µg/dL] and reproductive hormones [at serum lead levels over 30-40 µg/dL] and lowering vitamin D levels), brain (causing conditions such as brain lesions, cognitive deficits, and behavioural changes), and can cause anaemia. In children, low level (<10 µg/dL) lead exposure can result in several developmental disorders (accelerated skeletal growth, cognitive deficits and IQ decline, slowed growth and delayed sexual maturation) and higher levels (around 60-100 µg/dL) can manifest as colic (ATSDR, 2007b).

2.7.3 Cadmium

Acute cadmium intoxication is a potentially fatal, but very rare event (Bronstein et al, 2011); chronic exposure to cadmium presents a larger threat to human health (Thévenod et al, 2013). Cadmium has no known beneficial role in human metabolism.

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Cadmium is found in soil and ocean water, and up to 10% of the cadmium ingested from dietary sources, such as food and water, is absorbed by the body. It is readily absorbed (40-60%) through the inhalation of cigarette smoke and can be absorbed through the skin. Following exposure, cadmium binds to red blood cells and is transported throughout the body where it concentrates in the liver and kidneys; significant amounts are also found in the testes, pancreas, and spleen (Sigel et al, 2013). Cadmium is excreted slowly and may remain in the body for more than 20-30 years (Sigel et al, 2013; Thévenod et al, 2013). As it mimics zinc, cadmium is thought to exert its toxic activity by disrupting zinc metabolism; there are about 3000 different enzymes and structural proteins in human metabolism that require zinc for their activity and are potential targets of cadmium toxicity (Sigel et al, 2013). Cadmium interferes with the cellular balance of zinc, and nutritional zinc or iron deficiencies can increase cadmium absorption (Sigel et al, 2013; Thévenod et al, 2013). Chronic cadmium exposure can result in the accumulation of cadmium complexes in the kidney (potentially leading to renal failure), decreased bone mineralization, and decreased lung function; it is also a known human carcinogen (Sigel et al, 2013; ATSDR, 2012a; ATSDR, 2012b; Thévenod et al, 2013; Sinicropi et al, 2010).

2.7. 4 Arsenic

Although arsenic is not technically a “heavy metal,” this metalloid (an element with both metal and non-metal chemical characteristics) nevertheless holds significant potential for adverse health outcomes.

In both 2007 and 2011, arsenic topped the Agency for Toxic Substances and Disease Registry (ATSDR) Priority List of Hazardous Substances, which ranks hazardous substances based on their frequency, toxicity, and potential for human exposure from

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hazardous waste sites (ATSDR, 2011). It is one of the more commonly reported sources of unintentional intoxications (Bronstein et al, 2011). Arsenic occurs naturally in the environment as both inorganic (the less abundant, more toxic form) and organic (the less toxic, more abundant form) arsenic. The most common route of exposure in humans is consumption of arsenic-containing food or drinking water. Seafood contains the highest concentrations of organic arsenic; cereals and poultry are also sources. Arsenic can also be inhaled (the predominant route for occupational exposure) or absorbed through the skin (ATSDR, 2007a). Inorganic arsenic binds to hemoglobin in red blood cells once absorbed and is rapidly distributed to the liver, kidneys, heart, lungs, and to a lesser degree the nervous system, gastrointestinal (GI) tract, and spleen; it can also cross the placenta (Ibrahim et al, 2006). Some inorganic arsenic can be converted to organic arsenic compounds in the liver (monomethylarsonic and dimethylarsinic acids) that have less acute toxicity (Ibrahim et al, 2006; ATSDR, 2007a). Most inorganic and organic arsenic compounds are excreted by the kidneys, with a small amount retained in keratin-rich tissues (eg, nails, hair, and skin) (Ibrahim et al, 2006).

Arsenic binds and depletes lipoic acid in cells, interfering with the production of chemical energy (adenosine triphosphate -- ATP); it can also directly bind to and inactivate ATP (Ibrahim et al, 2006). Acute exposure to inorganic arsenic may cause nausea, vomiting, profuse diarrhea, arrhythmia, a decrease in red and white blood cell production, loss of blood volume (hypovolemic shock), burning or numbness in the extremities, and encephalopathy (Rusyniak et al, 2010; ATSDR, 2007a). Organic forms of arsenic have little acute toxicity compared to inorganic arsenic and arsine gas, the other two chemical forms of arsenic, which are more toxic (Ibrahim et al, 2006). Chronic inorganic arsenic exposure can result in anaemia, neuropathy, or liver

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toxicity within a few weeks to months (ATSDR, 2004; Ibrahim et al, 2006). Longer exposure (3-7 years) can also result in characteristic skin lesions (areas of hyperpigmentation or keratin-containing lesions) on the palms and soles of the feet. Severe exposure can lead to loss of circulation to extremities, which can become necrotic and gangrenous ("black foot disease") (Ibrahim et al, 2006; ATSDR, 2007a). Chronic exposure to arsenic has been associated with several types of cancer (skin, lung, liver, bladder, and kidney) (Ibrahim et al, 2006). Chronic exposure to dimethylarsinic acid, a form of organic arsenic, may cause kidney damage (ATSDR, 2007a).

2.7. 5 Other Metals

There are several other metals with documented toxicities and varying risk of unintentional overexposure.

Iron Iron toxicity is the most common metal toxicity worldwide (Crisponi et al, 2013; Kontoghiorghes et al, 2004). The classic symptom of iron overload, especially in the context of the disease hemochromatosis, is skin hyperpigmentation (to a bronze or grey color) due to deposits of iron and melanin complexes in the skin. The liver, as a primary source of iron storage, is particularly susceptible to overload and related damage (Siddique et al, 2012). Iron toxicity is also associated with joint disease (arthropathy), arrhythmia, heart failure, increased atherosclerosis risk, and increases in the risk of liver, breast, gastrointestinal, and hematologic cancers (Araujo et al, 1995; Nelson et al, 1995; Sahinbegovic et al, 2010; Ellervik et al, 2012; Kallianpur et al, 2004; Dongiovanni et al, 2011; Kremastinos et al, 2011).

Aluminum. Aluminum is ubiquitous in nature (it is the most abundant metal in the earth's crust) and naturally occurs in most foods and water; daily exposure through

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food, in most people, is 3-10 mg (Hewitt et al, 1990; Crisponi et al, 2013). However, occupational exposure to aluminum can cause significant toxicity, and aluminum toxicities are more frequently reported to poison control centers than are non-pesticide arsenic toxicities (Bronstein et al, 2011). Elevated levels of aluminum in the brains of some Alzheimer's patients is of unknown significance as to correlation and cause; data supporting the association is inconclusive, with more study required to determine if aluminum plays a causal role in Alzheimer's disease pathogenesis (Becaria et al, 2002; Lemire et al, 2011; Percy et al, 2011).

Copper Although copper plays an important role in human nutrition, toxicity at elevated exposure has been reported. Excessive copper (through overexposure or from copper metabolism diseases like Wilson's disease) can be neurotoxic (Wright et al, 2007), and acute unintentional copper toxicities are more frequently reported than those of arsenic (Bronstein et al, 2011).

Miscellaneous Acute manganese intoxication has also been infrequently reported to U.S. poison control centers (Bronstein et al, 2011). The release of depleted uranium into the environment (from armor-piercing ammunition) in regions like the Balkans and Middle East has been implicated in epidemics of leukemia, Kaposi sarcoma, and severe congenital defects (Shelleh, 2012).

Selenium

In addition to its role as a possible competitive inhibitor of mercury and lead absorption, selenium also increases toxic metal excretion. Moderate (100 mcg/day) increases in dietary selenium increased urinary excretion of stored mercury in long-term mercury-exposed Chinese residents (Li et al, 2012), and 100-200 mcg/day reduced blood and hair levels of arsenic in Chinese farmers with arsenic poisoning

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(Zwolak et al, 2012). Selenium also appears to mitigate the toxicity of some heavy metals, such as cadmium, thallium, inorganic mercury, and methylmercury, by modulating their interaction with certain biomolecules (Whanger, 1992). In another study, supplementation with 0.1 mg of selenium (in the form of selenomethionine) daily for 4 months led to a 34% reduction in levels of mercury detected in body hair. The authors of the study concluded that "mercury accumulation in hair can be reduced by dietary supplementation with small daily amounts of organic selenium in a short range of time" (Seppanen et al, 2000).

Silicon

Data from preliminary human studies reveal that naturally-occurring dissolved silicon from mineral waters appears to antagonize the metabolism of aluminum, potentially reduce Alzheimer's risk, and support cognitive function (Gillette et al, 2007). In human subjects, soluble silicon (orthosilicic acid) decreases aluminum absorption from the digestive tract and decreases its accumulation in the brain (Jurkic et al, 2013). In one study, Alzheimer's patients drank up to 1 L of mineral water daily (containing up to 35 mg of silicon/L) for 12 weeks. Over the study period, urinary excretion of aluminum increased without affecting urinary excretion of the essential metals iron and copper. In addition, there was a clinically relevant improvement in cognitive performance in at least 3 out of 15 individuals (Davenward et al, 2013).

Another source of orthosilicic acid studied for their metal reducing properties are compounds called zeolites. Zeolites are aluminium/silicon oxide-based crystalline compounds with adsorbent properties that have broad industrial applications and are finding applications in medicine (Montinaro et al, 2013; Beltcheva et al, 2012). Inclusion of zeolite (as the zeolite clinoptilolite) in high-lead diets of laboratory mice

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reduced tissue lead concentration by 77-91%, increased the percentage of healthy red blood cells, and reduced chromosomal damage (Topashka-Ancheva et al, 2012; Beltcheva et al, 2012). A clinical study on 33 men evaluated the ability of the zeolite clinoptilolite to increase heavy metal urinary excretion (Flowers et al, 2009). To be included in the trial the men had to test positive, above a predetermined threshold, for at least four of the nine metals in a urinary test panel (ie, aluminum, antimony, arsenic, bismuth, cadmium, lead, mercury, nickel, and tin). The men were given either 15 drops of a clinoptilolite water suspension or placebo suspension twice daily for a maximum of 30 days. Significant increases in the urinary excretion of all 9 metals were observed in the men taking clinoptilolite as compared to placebo without a negative impact on electrolyte profiles. It has been hypothesized that the biological activity of some zeolites may be attributed to their orthosilicic acid releasing properties (ie, they are a source of orthosilicic acid) (Jurkic et al, 2013).

2.8 Risk Factors for Toxic Metal Exposure

Exposure of the general population to toxic metals may come from the environment or home and can be acute or chronic. It may result from contaminated food, air, water, or dust; living near a hazardous waste site or manufacturing plant that releases metal contaminants; overexposure to metal-containing pesticides, paints, or cosmetics; or improper disposal or clean-up of toxic metal-containing items (such as a broken thermometer).

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Exposure risks for specific metals include:

Lead:

- Lead-containing plumbing (lead pipes or plumbing solder. In 2007, it was estimated that less than 1% of the public water systems in the United States had lead levels above 5 µg/L) (ATSDR 2007b)
- Lead-based paints (in buildings built before 1978; this is the predominant source for children) (EPA, 2013)
- Leaded gasoline (although banned in the United States in 1995 for automobiles, previous usage has widely dispersed it in the environment) (Miranda, 2011)
- Foods grown in lead-rich soil (ATSDR, 2008a)

Mercury:

- Eating fish or shellfish contaminated with methylmercury the Food and Drug Administration [FDA] has set a maximum permissible level of 1 part of methylmercury in a million parts of seafood [1 ppm] (ATSDR, 2001). Ocean fish commonly high in mercury include shark, swordfish, king mackerel, and tilefish (Defilippis et al, 2010). Levels of mercury above 1 ppm have also been found in predatory and bottom-dwelling freshwater fish (including bass, walleye, and pickerel) from mercury-contaminated waters (ATSDR, 2001)
- Breathing contaminated workplace air or skin contact during use in the workplace (certain medical and dental treatments as well as chemical or other industries that use mercury) (ATSDR, 2000)

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- Release of mercury vapor from dental amalgam fillings (although the FDA deems amalgam fillings safe) (Bernhoft et al, 2012; Jang et al, 2011; Rusyniak et al, 2010; FDA, 2009)
- Contact with elemental mercury from the following household devices: thermometers (the amount of elemental mercury from a broken thermometer spilled in a small, enclosed space can cause systemic toxicity if not properly cleaned up), fluorescent and mercury vapor lamps, thermostats, manometers/barometers, and wall switches manufactured before 1991 (Caravati et al, 2008)
- Skin-lightening products and antiseptics that contain mercury salts (Park et al, 2012)

Arsenic:

- Groundwater near arsenic-containing mineral ores
- Wood preservatives (found in treated wood products manufactured before 2004) and antifouling paints
- Some insecticides, herbicides (weed killers and defoliants), fungicides, cotton desiccants, paints and pigments
- Seafood (shellfish, certain cold water and bottom-feeding finfish, and seaweed contain organic arsenic compounds with low acute toxicity) (ATSDR, 2007a)

Cadmium:

- Tobacco smoke (cadmium can concentrate in tobacco leaves)

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- Eating foods containing cadmium (levels are highest in grains, legumes, and leafy vegetables, and cadmium can bioaccumulate in fish and shellfish)
- Contact with cadmium from household products (electric batteries and solar panels) (Nogué et al, 2004; ATSDR, 2012a

2.9. Signs and Symptoms

Heavy metal toxicity can cause a variety of signs and symptoms. While manifestations of toxicity vary among the many toxic metals, several symptoms are often observed and may be indicative of heavy metal toxicity (Adal et al, 2013): Nausea, Vomiting, Diarrhoea, Abdominal pain, Central nervous system dysfunction, Heart problems, Anaemia ,Fingernail or toenail discoloration (Mee's lines; usually appearing as white stripes running horizontally across the nails)

Acute metal toxicity can be a life-threatening medical emergency that may require aggressive treatment in a hospital setting. If you suspect you have been exposed to a toxic metal, seek medical attention immediately.

2.10 Analytical technique in heavy metal analysis

2.10.1 Inductively Coupled Plasma (ICP)

This is an analytical technique used for the detection of trace metals in environmental samples (Worley et al, 2011). The goal of ICP is to get the elements emit characteristic wavelength of specific light which then can be measured. Samples are decomposed to neutral elements in high temperature argon plasma and analysed based on their mass to charge ratios. Aqueous samples are introduced by a way of a nebulizer which aspirates the sample with high velocity argon, forming a fine mist.

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The aerosol then passes into a spray chamber where larger droplets are removed via a drain (Worley et al, 2011). Solid samples are introduced into the ICP by a laser ablation system (www.cee.vt.edu/ewr/environmental/teach/smprimer/icp/icp.html). The non-availability of the equipment could not make it possible for the technique to be used.

2.10.2 Instrumental Neutron Activation Analysis (INAA)

INAA is also an analytical tool based on the measurement of characteristic radiations emitted from radionuclide's formed directly or indirectly by neutron irradiation/bombardment of the material of interest (IAEA, 2001). It is capable for simultaneous multi-elemental analysis with no or minimal chemical treatment of samples. It is a non-destructive method with adjustable parameters that can be exploited for maximum sensitivity for the desired element. With these strengths, a major setback for its use in this study is its inability to detect lead (Pb), a key element known to be heavy metal. In addition, it is time consuming due to the different irradiation, decay and counting times for the elements depending on their half-lives.

2.10.3 X-Ray Fluorescence Spectroscopy (XRF)

X-ray fluorescence (XRF) spectrometry is an elemental analysis technique with broad application in science and industry. XRF is based on the principle that individual atoms, when excited by an external energy source, emit X-ray photons of a characteristic energy or wavelength. By identifying the photon peaks and counting the number of photons of each energy emitted from samples, the elements present can be identified and quantitated.

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Modern XRF instruments are capable of analyzing solid, liquid, and thin-film samples for both major and trace (ppm-level) components. The analysis is rapid and usually sample preparation is minimal or not required at all.

The identification of elements by X-ray methods is possible due to the characteristic radiation emitted from the inner electronic shells of the atoms under certain conditions. The emitted quanta of radiation are X-ray photons whose specific energies permit the identification of their source atoms. To understand this phenomenon, we must first look at how X-rays are generated.

When an electron beam of high energy strikes a material, one of the results of the interaction is the emission of photons which have a broad continuum of energies. This radiation, called *bremsstrahlung*, or "braking radiation", is the result of the deceleration of the electrons inside the material.

Another result of the interaction between the electron beam and the material is the ejection of photoelectrons from the inner shells of the atoms making up the material. These photoelectrons leave with a kinetic energy (E-φ) which is the difference in energy between that of the incident particle (E) and the binding energy (φ) of the atomic electron. This ejected electron leaves a "hole" in the electronic structure of the atom, and after a brief period, the atomic electrons rearrange, with an electron from a higher energy shell filling the vacancy. By way of this relaxation the atom undergoes *fluorescence*, or the emission of an X-ray photon whose energy is equal to the difference in energies of the initial and final states. Detecting this photon and measuring its energy allows us to determine the element and specific electronic transition from which it originated (Jenkins et al, 1988: 4-6, Anzelmo et al, 1987 Part 1). Herein lies the basis for XRF spectrometry, where elements may be quantitated

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based on the rate of emission of their characteristic X-rays from a sample that is being excited.

Any of the electrons in the inner shells of an atom can be ejected, and there are various electrons in the outer shells that can “drop” to fill the void. Thus there are multiple types of allowed transitions that occur which are governed by the laws of quantum mechanics, each transition having its own specific energy or line (Jenkins et al, 1988: 6). The three main types of transitions or *spectral series* are labelled K, L, or M, corresponding to the shell from which the electron was initially removed. K series lines are of the highest energy, followed by L and then M. Within the series, the specific transitions are denoted by the subscripts α, β, γ, etc. to denote which upper energy shell was involved in the relaxation and finally a numerical subscript to indicate the quantum state within that upper energy shell. For example, the Mo Kα1 transition yields a photon of wavelength 0.071 nm. (Jenkins et al, 1988 p. 4) It is important to note that only the very highest resolution spectrometers could resolve Kα1 and Kα2 lines, so for practical purposes in X-ray spectrometry only the Kα line would be mentioned (Skoog et al, 1998: 275, once the excitation energy of the incident electron beam exceeds the Mo K transition energies these lines begin to appear in the tube spectrum.

Fluorescence, however, is not the only process by which an excited atom may relax. It competes with the Auger effect, which results in emission of a second photoelectron to regain stability. The relative numbers of excited atoms that fluoresce are described by the *fluorescence yield*, which increases with increasing atomic number for all three series (Jenkins et al, 1988: 6).

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High energy electrons are not the only particles which can cause ejection of photoelectrons and subsequent fluorescent emission of characteristic radiation. High-energy X-ray photons can create the same effect, allowing us to excite a sample with the output of an X-ray tube or any source of photons of the proper energy. In fact, in some applications of XRF spectrometry, X-rays from a tube are used to excite a secondary fluoresce, which emits photons that in turn are used to excite the sample.

When X-rays impinge upon a material, besides being absorbed, causing electron ejection and subsequent characteristic photon emission, they may also be transmitted or scattered. When an X-ray is scattered with no change in energy this is called *Rayleigh* scattering, and when a random amount of energy is lost the phenomenon is *Compton* scattering. Scattered X-rays are usually problematic in XRF, creating high levels of background radiation (Anzelmo et al, 1987 Part 1).

Since only the inner electron shells are involved in the emission of X-rays, the wavelengths are independent (within our ability to measure) of the state of chemical bonding, which involves the outer-most electron shells only. One exception to this rule involves low-Z elements with fewer electrons. The overall lack of chemical shifts allows the analyst to determine the elemental composition of the sample, whether the elements are present in their pure forms or as compounds (Skoog et al, 1998: 275).

Detecting this photon and measuring its energy allows us to determine the element and specific electronic transition from which it originated. This lays the basis for X-ray fluorescence (XRF) technique, where elements may be quantitatively categorized and qualitatively determined based on their rate of emission.

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This technique which is suitable for the research work could not be used due to its unavailability in the laboratories around, resulting into using AAS.

2.10.4 Atomic Absorption Spectrometry (AAS)

This is another analytical technique used for elemental analysis. It is an analytical procedure that employs the absorption of optical radiation (light) by ground state, free atoms in the gaseous state (free atoms are formed from the samples by an "atomizer" at high temperatures) for both quantitative and qualitative determination of chemical elements. The technique makes use of absorption spectrometry to assess the concentration of an analyte in a sample (http://en.wikipedia. org/wiki/atomic _absorption spectroscopy). In the assessment of heavy metal pollution in soils along major roadside in Botswana (Mmolawa, et.al, 2011), pollutants such as Al, Co, Cu, Fe, Pb, Ni, Zn and Mn, were determined using flame absorption atomic spectrometry (FAAS).

AAS as an elemental analysis technique has the significant advantage in many cases of being independent of the chemical form of the element in the sample. As a technique also, a given element can be determined in the presence of other elements without interference. The sample preparation techniques could also be time consuming for large sample sizes and availability of appropriate gas combinations for the determination of some elements (Atiemo, et.al, 2010).

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*2.10.4.1 The Basic Principle of Atomic Absorption Spectrometry (*AAS)

Design of spectroscopic systems is based on the fundamental principle of light absorption by absorbing species-the Beer Lambert law.

The basic principle of atomic absorption spectroscopy can be expressed by three simple statements

-All atoms can absorb light

-The wavelength at which light is absorbed is specific for each element. If a sample containing nickel for example, together with elements such as lead and copper is expressed to light at the characteristic wavelength for nickel, then only the nickel atoms will absorb this light.

-the amount of light absorbed at this wavelength will increase as the number of atoms of the selected element in the light path increases and is proportional to the concentration of absorbing atoms.

The relationship between the amount of light absorbed and the concentration of the analyte present in known standards can be used to determine unknown concentrations by measuring the amount of light they absorb. An atomic absorption spectroscopy is simply an instrument in which these basic principles are applied to practical quantitative analysis (ASTM international, 2006).

Figure 2.1 is a schematic of a typical atomic absorption spectrometer. There are four major components–The light source, atomization system, the spectrometer and the

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detection system

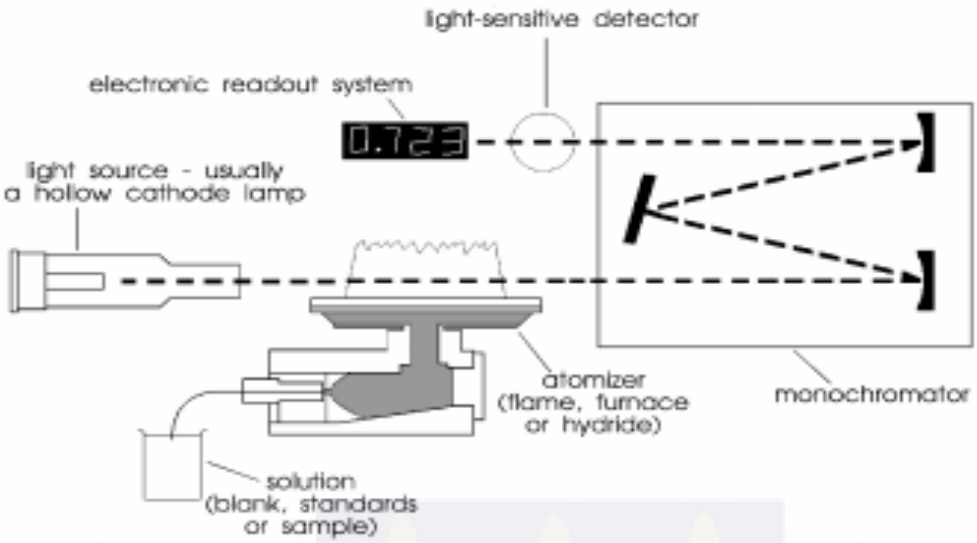

Figure 2.3 Schematic of a typical atomic absorption spectrometer

A basic atomic absorption instrument consists of the following key components:

- A light source used to generate light at the wavelength which is characteristic of the analyte element. This is most often a hollow cathode lamp, which is an intense narrow line source (other sources being Electrodeless Discharge Lamps (EDLs) or boosted discharge hollow cathode lamps (Ultra lamps)).
- An atomizer to create a population of free analyte atoms from the sample. The source of energy for free atom production is usually heat– most commonly in the form of an air/acetylene or nitrous-oxide/acetylene flame. The sample is introduced as an aerosol into the flame and the burner is aligned in the optical path so that the light beam passes through the flame, where the light is absorbed.

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- An optical system to direct light from the source through the atom population and into the monochromator.
- A monochromator to isolate the specific analytical wavelength of light emitted by the hollow cathode lamp from the non-analytical lines including those of the fill gas.

- A light-sensitive detector (usually a photomultiplier tube) to measure the light accurately. Suitable electronic devices which measure the response of the detector and translate this response into useful analytical measurements. The instrument readout may be one of several types. Older instruments used meter readout devices. These have been replaced by modern instrumentation using direct computer interfacing.
    - At its most basic level, the general analytical procedure is straight-forward:
    - Convert the sample into solution, if it is not already in solution form.
    - Make up a solution which contains no analyte element (the analytical blank).
    - Make up a series of calibration solutions containing known amounts of analyte element (the standards).
    - Atomize the blank and standards in turn and measure the response for each solution.
    - Plot a calibration graph showing the response obtained for each solution as shown below.
    - Atomize the sample solution and measure the response.
    - Determine the concentration of the sample from the calibration, based on the absorbance obtained for the unknown.

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There are two basic types of atomic absorption instruments: single-beam and double-beam.

2.10.4.2 Light sources in atomic absorption spectrophotometer

Light sources are generally of two types. You'd be familiar with 'continuum light sources' such as Sun or a light bulb which emit electromagnetic radiation in the wavelength range from about 250 to 700 nm in the visible region which we see as normal white light. The white light comprises of several different wavelengths which constitute the colours of the rainbow. The other type of light sources is 'line sources' which emit light of a specific wavelength and it is such light sources which are used in Atomic Absorption Spectroscopy. Now you shall be introduced to such light sources

2.10.4.2.1 Hollow Cathode Lamps

A Figure 2.4 is a hollow cathode lamp gives a high intensity, narrow line wavelength of element to be determined

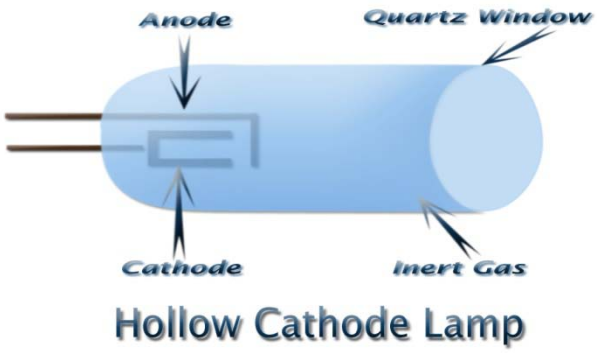

Figure 2.4 Hollow Cathode lamp

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The hollow cathode lamp consists of a glass cylinder filled with an inert gas usually Argon or Neon at low pressure. The cathode is made from metal which is to be determined. The emission line of the lamp corresponds with the absorption wavelength of the analyte. The end window of the lamp is usually made of Quartz or Pyrex that transmits the spectral lines of the element to be determined.

Following stages are involved in light emission from Hollow cathode lamp:

- **Sputtering –** filled gas is ionized when potential difference is applied between the anode and the cathode. Positively charged inert gas ions strike the negatively charged cathode and dislodge metal atoms.
- **Excitation –** sputtered metal atoms are excited to impact with the ionized gas
- **Emission –** light of wavelength specific to the element comprising the cathode is emitted when the atom decays from the excited state to the normal state

Hollow cathode lamps have a shelf life as well as usage lifetime defined in milliampere hours. Increasing current increases lamp intensity but excessive current reduces lamp life and also results in self-absorption broadening i.e., atoms in the hollow cathode lamp begin to absorb light emitted from the hollow cathode lamp itself. This leads to lower absorbance and reduction in the linear range of calibration curve.

2.10.4.2.2 Multielement Hollow Cathode Lamps

The cathode of multielement lamps is made from alloying compatible elements without overlapping line spectra. Examples of such lengths are Ca-Mg,Cu-Fe-Ni, Cu-

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Fe-Mn-Zn, etc. All elements of multielement hollow cathode lamps can be determined sequentially without need for change of lamps in between. Multielement lamps provide advantages of cost, speed of analysis but the sensitivity is lower in comparison to individual element determination by single element lamp

2.11 Nature of Atomic and Ionic Spectra

In order to understand the atomic absorption process, one must first understand the Bohr model of the atom which describes the structure of the atom and its orbitals. The atom consists of the central core or nucleus, made up of positively charged protons and neutral neutrons. Surrounding the nucleus in defined energy orbitals are the electrons. All neutral atoms have an equal number of protons and electrons. Each of these electron orbital's has an energy associated with it–in general, the further away from the nucleus; the more readily can the electron be removed. Atomic spectroscopy involves energy changes in these outer electrons.

When the atom and its associated electrons are in the lowest energy state, Eo, the atom is said to be in the ground state. Atoms can absorb discrete amounts of heat or light at certain discrete wavelengths, corresponding to the energy requirements of the particular atom. When energy is added to the atom as a result of absorption of light, heat or collision with another particle (electron, atom, ion or molecule), one or more changes may occur.

The energy absorbed may simply increase the kinetic energy of the atom or alternatively, the atom may absorb the energy and become excited. The permitted energy levels are finite and well defined, but an electron may be made to change to another level if the atom absorbs energy equal to the difference between the two

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levels. When this occurs, the electron moves to a higher energy level, such as E1. This atom is now said to be excited.

Atomic absorption is the process that occurs when a ground state atom absorbs light of a specific wavelength and is elevated to a higher energy level (i.e. the process of moving electrons from the ground state to an excited state). Sodium atoms, for example, absorb light very strongly at 589.0 nm, because light at this wavelength has exactly the right energy to raise the sodium atom to another electronic state. This electronic transition is quite specific for sodium; atoms of any other element have different energy requirements and they cannot absorb light at this wavelength. If the sodium atom is in the 'ground state' when it absorbs light, it is transformed into an excited state–it is still a sodium atom, but it contains more energy.

The energy levels of each atom are quantized according to the number of protons and electrons present. Since each element has a unique set of electrons and protons, each element also has a unique set of energy levels. Usually these energies are measured in relation to the ground state, and a particular excited state for sodium, for example, may be 2.2 eV (electron volts) above the ground state. This means that an atom in the excited state contains 2.2 eV more energy than a ground state atom which, by convention, is ascribed an arbitrary energy of zero. An element may have several electronic energy states.

The wavelength of the absorbed light is proportional to the spacing between the energy levels–this is characteristic of the element itself. The wider the spacing between the energy levels, the shorter the wavelength of light energy absorbed. Each transition between different electronic energy states is characterized by a different energy and hence by a different set of wavelengths at which the atom will also absorb.

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These characteristic wavelengths also correspond to those wavelengths at which an element will emit–the process of being at a higher energy level and relaxing to the ground state. These wavelengths are sharply defined and when a range of wavelengths is surveyed, each wavelength shows as a sharp energy maximum (a spectroscopic 'line'). Atomic spectra are distinguished by these characteristic lines. Lines which originate in the ground state atom are most often of interest in atomic absorption spectroscopy; these are called 'resonance lines'. Transitions from one excited state to another yield non-resonance lines.

The atomic spectrum characteristic of each element comprises a number of discrete lines, some of which are resonance lines. Most of the other lines arise from excited states, rather than from the ground state. Since the resonance lines are much more sensitive and since most atoms in a practical atomizer are found in the ground state, these excited state lines are not generally as useful for atomic absorption analysis.

2.12 Ionization

Ionization may occur when the temperature of the flame is high enough to remove the outer electron from the atom. Atoms that undergo ionization reaction are not available to undergo atomic absorption; therefore the measured signal is decreased. Ionization occurs when an anion or cation in the sample reacts with the analyte to alter the rate of formation of the free ground state analyte atoms. They can be either enhancement reactions, giving higher absorbance or suppression reactions giving lower absorbance. Ionization of the analyte reduces sensitivity and causes upward curvature at high concentrations. Thus, the characteristic upward curvature of the calibration curve when analyte ionization is significant, indicates that the effect of ionization is more severe at lower concentrations. At higher analyte concentrations–ion and electron

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recombination's are more probable, resulting in a greater proportion of ground state atoms being available for absorption. The hotter the flame, the greater the degree of ionization. The degree of ionization is different for each element, depending on the energy required to remove the electrons. Easily ionisable elements such as the group I elements are most susceptible to these effects.

Analyte ionization can be suppressed by adding a large concentration of a more easily ionized element such as sodium, potassium (e.g.: 0.2% KCl) or cesium at concentrations between 2000 and 5000 mg/L. This creates an excess of electrons in the flame and effectively suppresses ionization of the analyte.

2.13 Atomic Emission

Absorption lines used in atomic absorption analysis are due to transitions from the ground state to a higher energy level. Atoms in the excited state are generally unstable and will rapidly revert to the ground state, losing the acquired energy in the process. Emission lines are produced when these transitions from higher energy states to lower energy states occur. The wavelengths at which these energy shifts take place are exactly the same for both emission and absorption (Welz, 1985)

Thus, atomic emission spectroscopy is a process in which the light emitted by excited atoms or ions is measured. The emission occurs when sufficient energy (which may be thermal, light or electrical) is provided to excite a free atom or ion to a higher unstable energy state (the atomic absorption process). At low temperatures, few atoms are excited. As the temperature increases to about 2000 K, some easily excited elements such as those of the alkali elements can be detected. As seen in absorption, the wavelength of emitted light is proportional to the spacing of the energy levels. Since each element has a unique set of energy levels, each element also has a unique

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set of wavelengths at which it will emit energy. Thus, the wavelengths of light emitted by the atoms or ions are specific to the elements which are present in the sample.

It is also possible to determine the concentration of analyte that is present in a sample by measuring the amount of light emitted and comparing this value with the amount of light emitted by known standards.

The basic instrument configuration for atomic emission is essentially the same as that for atomic absorption, except that a primary light source is not required. The most critical component in an atomic emission instrument is the atomization source–this must provide sufficient energy to atomize the sample and excite the free atoms. The earliest energy sources for excitation have been air/acetylene and nitrous-oxide/acetylene flames. Most atomic absorption instrumentation are provided with the capability for measurements by atomic emission. Selected elements such as Li, Na, K and the other alkali elements are easily measured by atomic emission because the excited states of these elements can be populated from the energy supplied by the flame.

However, the flame types available in atomic absorption instrumentation generally lack sufficient thermal energy to be truly effective at creating large numbers of excited atoms or ions. In addition, the monochromators used in most AA systems do not have the resolution required to isolate the selected emission wavelength from the many emission wavelengths which may be emitted by the sample. Because of these limitations of atomic emission, the technique does not enjoy the popularity of atomic absorption.

The development of Inductively Coupled Plasma (ICP) as a source for atomic emission has changed this dramatically. The temperature of the sample within the argon plasma of an ICP-AES system can reach between 5500 to 8000 K. These

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temperatures allow complete ionization of elements, minimizing chemical interferences, and providing ample thermal energy to excite most of the free atoms in the sample. The ICPAES system provides a wide dynamic range and minimal chemical interferences. However, the optics design of an ICP-AES must have much greater resolution than that of an atomic absorption spectrometer so that the emission wavelength of interest can be isolated from the many wavelengths emitted by the sample within the plasma.

The ICP-AES system eliminates many of the problems associated with previous emission sources and has resulted in a dramatic increase in the use of emission spectroscopy as a technique for elemental analysis.

2.14 The Absorbance - Concentration Relationship

Once the absorbance is measured, this value can then be related to the concentration of an element in solution. The relation between light absorption and analyte concentration is called the Beer-Lambert law:

Lambert's Law states that the portion of light absorbed by a transparent medium is independent of the intensity of the incident light, and each successive unit thickness of the medium absorbs an equal fraction of the light passing through it.

Beer's Law states that the light absorption is proportional to the number of absorbing species in the sample. Effectively for AA, this means that the amount of energy (light) absorbed is proportional to the concentration of atoms in the atomizer. Thus if a concentration of atoms 'c' produced an absorbance 'a', a concentration '2c'would produce an absorbance '2a'.

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The combined Beer-Lambert law can be expressed as:

Log10Io/It = absorbance = a * b * c

Where:

Io = incident light intensity

It = transmitted light intensity

a = absorption coefficient (absorptivity)

b = length of absorption path

c = concentration of absorbing atoms

For a given set of conditions, a and b are constants. The path length, b, will change if different burners are used, as an air/acetylene burner has a path length of 100 mm compared to 60 mm for the nitrous oxide/acetylene burner. If this expression is plotted, and a curve of absorbance versus concentration is drawn,

Beer's Law predicts that a straight line will result. In practice, we find that several factors relating to spectral effects and instrumental design can combine to cause deviations from the linear calibration, especially at higher concentrations.

A further significant issue in atomic absorption is the residence time of atoms in the light path of the instrument. Typical flame residence times are only milliseconds. Longer residence times are usually associated with greater absorbance. This is used to good effect in the operation of the Atom Concentrator Tube (ACT-80).

2.15 Atomization

Atomization is the process by which atoms are made available for absorbance measurement. Atomic absorption analysis is dependent on creating a supply of free analyte atoms in the ground state and exposing this atom population to light of the characteristic wavelength for that element. As with other spectrochemical techniques,

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AAS is used to determine element concentrations, usually in liquid form. AAS is best suited to the analysis of elements in aqueous solutions of a dissolved or diluted sample, or samples diluted with solvents such as organic solvents. Since the development of AAS a number of different atomizer techniques have been developed. The three major classifications of atomizers are flames, graphite furnaces and vapour generation (Dean et al 1969).

2.15.1 Flame Atomization

The flame atomization systems used in atomic absorption convert the analyte solution into free atoms in the optical path via successive stages, as illustrated below. The primary aim of the sample introduction system is to generate an aerosol of the sample in the fuel mixture. This requires the production of an aerosol with a sufficient number of small droplets and to introduce a portion of the sample in the flame without experiencing difficulties such as nebulizer or burner blockage. The usual means of sample introduction is to use a nebulizer to create the aerosol and a spray chamber to filter larger droplets from the aerosol.

The nebulizer draws the solution in through the capillary. The stream of solution passing through the venture strikes the impact bead which breaks the stream of liquid into an aerosol of various droplet sizes. The spray chamber removes the large droplets and mixes the remainder with the flame gases. The spray chamber plays a crucial role in promoting intimate mixing of the nebulizer aerosol with the fuel. This mixture passes into the burner. In order to obtain maximum sensitivity, it is necessary to pass as much as possible of the light from the hollow cathode lamp through the flame. It is therefore necessary to adjust the burner position for each separate analysis so that the maximum population zone of free atoms coincides with the optical path. All atomic

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absorption instruments incorporate simple burner controls which allow the analyst to adjust the burner position in the vertical, horizontal and rotational planes until the maximum absorbance can be obtained. The heat of the flame evaporates the solvent, near the base of the flame, converting the aerosol droplets into very small solid particles. These particles are fused or melt, and are vaporized to form molecules. These dissociate to produce the mostly free ground state atoms in the optical path. Most samples used in flame atomic absorption are nebulized into an aerosol–a very fine mist of sample droplets. This diagram illustrates the processes that occur when the aerosol is introduced to the flame–the aerosol is quickly desolated, any solids present are fused, molecules decomposed and elements atomized in a very short time.

2.15.2 Monochromator

In practice, all but the most elementary monochromators consist of an entrance slit to confine the source radiation to a usable area, mirrors to pass the light through the system, a dispersing element to spread the source radiation into its component wavelengths and an exit slit to select the wavelength for analytical measurement. Since the hollow cathode lamp emits many narrow emission lines, the sole function of the monochromator is to isolate a single atomic resonance line from the total spectrum of lines emitted by the hollow cathode lamp. In effect, it is an adjustable filter which selects a specific, narrow region of the spectrum for transmission to the detector and rejects all wavelengths outside this region. Essentially the monochromator is tuned to select a particular wavelength of light much as you would tune a radio to a par The ability to discriminate between different wavelengths (usually referred to as resolution) is thus a very important characteristic of the monochromator. Monochromators designed for emission techniques need very high resolution due to

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the complexity of the emission spectra generated by a high temperature source such as the Inductively Coupled Plasma (ICP). An ICP monochromator can isolate wavelength regions less than 0.01nm; however, for atomic absorption spectrometers, a typical requirement is about 0.2 nm 'bandpass'. Other designs use different arrangements of the optical components but the operating principle is the same for all of the particular radio station (Pitts et al 1970)

2.15.3 Detectors

Once the proper atomic resonance line has been isolated by the spectrometer, the detector and its associated electronics are used to measure the intensity of the atomic absorption or emission. The detector universally used is the photomultiplier tube. This has high sensitivity, a wide dynamic range and can be used across the complete wavelength range required for atomic absorption analysis.

The photomultiplier tube is a vacuum tube that produces an electrical signal which is proportional to the intensity of the light which reaches the device. Light admitted through a window in the photomultiplier tube falls directly onto a photosensitive material–the photocathode. The cathode is coated with a material which emits electrons whenever it is illuminated. The higher the intensity of the incident light the greater the number of electrons emitted. The electrons emitted are accelerated towards an adjacent electrode, maintained at a positive electrical potential with respect to the cathode. This is called a dynode. When each electron reaches the dynode, it liberates a number of secondary electrons which are in turn attracted to another dynode, emitting even more electrons. This is the multiplier process that gives the photomultiplier its Name. A dynode chain of between 9 to 16 stages is usually fitted inside the PMT, causing an increase in the electron current generated at the cathode. As many as 108

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secondary electrons may be collected as the result of a single photon striking the photocathode.

The electrical current measured at the anode is then used as a relative measure of the intensity of the radiation reaching the PMT. Thus the light intensities which are obtained in atomic spectroscopy lead to an electric current of useful magnitude which can be further amplified to provide the required quantitative measurement.

The major advantage of the PMT over other detection devices are that it can be used to measure light over the complete wavelength range of analytical interest, it can amplify very weak incident light levels and it has a wide dynamic range.

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CHAPTER THREE

METHOD

3.1 Sampling

The grinding plates mostly used in Ghana are made from India, Nigeria and Ghana. This information was generated from the market survey conducted on the kind of corn-mill plates being used in Ghana. Hundred (100) milling shops visited in Accra, 85% used locally- manufactured con-mill plate and the remaining 15% used foreign plates. Ghanaian made plates are patronised more than that of Indian and Nigerian due to their low price (Kwofie and Chandler, 2006). Since the grinding plates were from the same producer, a pairs of Ghanaian, Indian and Nigerian corn-mill grinding plates were purchased from the market in Accra Central for this work. The mode of selection of these grinding plate samples was at random. The plates are in a form of a disc having a diameter of about 30cm and a hollow core diameter of about 11cm. The plates are not of uniform thickness. The thickness ranges from about 10mm at the outer circumference and tapers down to about 3 mm at the centre. In addition the plate surface has grooves/striations for effective grinding/milling operation as shown in Fig 3.1.

Figure 3.1 Corn-Mill grinding Plate

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The maize used for this work comes from the same farm at Sogakope in the Volta region. Maize was chosen for this study because Maize is a staple food in Ghana and is grown in many parts of the tropics for both human and animal consumption. It is the most popular of all grain crops and it is grown all over the country. Maize is processed into flour which is used in the preparation of many local foods such as Koko, Akple", "Banku","kenkey","apreprensa" "abolo" "tuo zaafi" and maize porridge (Lokko et al, 2004).

3.2 Sample preparation

Figure 3.2 Agate mortar and pestle used to grind maize

Figure 3.3 Corn mill machine used to grind maize

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Fig. 3.4 Milled maize in zip polythene bag

3.2.1 Milling

The milling process (Fig. 3.2) was carried out using three different milling machines. The Ghanaian, Indian and Nigerian made plate were each place in each of the milling machine, 2 Kg weight of the maize sample was milled in each of the three milling machine immediately after the insertion of the grinding plates into the machines. The plates were left in the machine to be used for milling for thirty days after which a second set of 2 kg weight was taken through the same process. This process was repeated for the third and fourth times to assess the wearing rate of the grinding plate. The milling machines are located at Dome market in Ga-East District of Accra.

The weight of grinding plate was measured and recorded (Table 3.2) after every thirty (30) days before the next sample of 2 kg maize was milled.

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Agate mortar and pestle was used to pulverize 50 g of the corn into flour. This pulverized sample was used to ascertain the original concentration of metals in the maize sample.

3.2.2 Grinding plate

The grinding plates were thoroughly cleaned with de-ionized water after which a small piece of 1.0 g was cut out for elemental analysis using Atomic absorption spectrometry techniques. AAS involved several processes in sample preparation, among these include digestion.

Digestion protocol adopted for this work

The 1.0 g cut out of each plate sample were put into 37% HCl for 30 minute and then washed with de-ionized water. This is done to avoid any external contamination due to handling and exposure to dust. The plate sample was left in 25ml (95% HCL) for 3 days to dissolve. It was digested with aqua-regia (3 ml 65% HNO3: 1ml 37% HCl) in high borosilicate glass vessel on a hot plate at 95°C for 3hours. The digested samples were allowed to cool at room temperature. The sides of the beakers were washed with de-ionised water and made to a final volume of 30 ml. The digested solutions were filtered into test-tubes and kept for elemental analysis (VARIAN. Publication No 85-100009-00 Revised March 1989).

3.2.3 Corn flour

The corn flour (Fig. 3.3) was sieved through the 250 um nylon sieve and store in a polyethylene (PE) bags. Care was taken at each stage of preparation to avoid contamination. Sample collected were thoroughly mixed to make sure that

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representative samples were obtained. The corn flour from the milling after every 30 days were labelled 1st milling, 2nd milling, 3rd milling and 4th milling consecutively. The plate from Ghana, India and Nigeria in each milling, grind four of 2 kg maize samples. A total of twelve samples were then obtained.

Digestion:

For digestion of corn flour, 0.5 g was dissolved in 25ml and digested with aqua-regia (3ml 65% $HNO_{3:}$ 1ml 37% HCl) in a high borosilicate glass vessel for 3 hours on a hot plate at 95^0C. The digested samples were allowed to cool at room temperature. The sides of the beakers were washed with de-ionised water and made to a final volume of 30ml. The digested solutions were filtered into test-tubes and stored for elemental analysis (VARIAN. Publication No 85- 100009-00 Revised March 1989).

3.3 Reagents

Reagents used were of analytical grade, supplied by British Drug House (BDH) and Sigma. De-ionised water used was produced by the Nuclear Chemistry and Environmental Research Centre, GAEC. Other reagents include: Trioxonitrate (v) acid (HNO3), Hydrochloric acid (HCl)

3.4 Materials and Equipment

Fast sequential Atomic absorption spectrometer model AA240FS equipment were calibrated appropriately before measurement. Others are: Pre-treated test tubes, Hand gloves, Filter paper, Self- press polythene bags, Hot plate and conical flask.

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3.5 Elemental Analysis

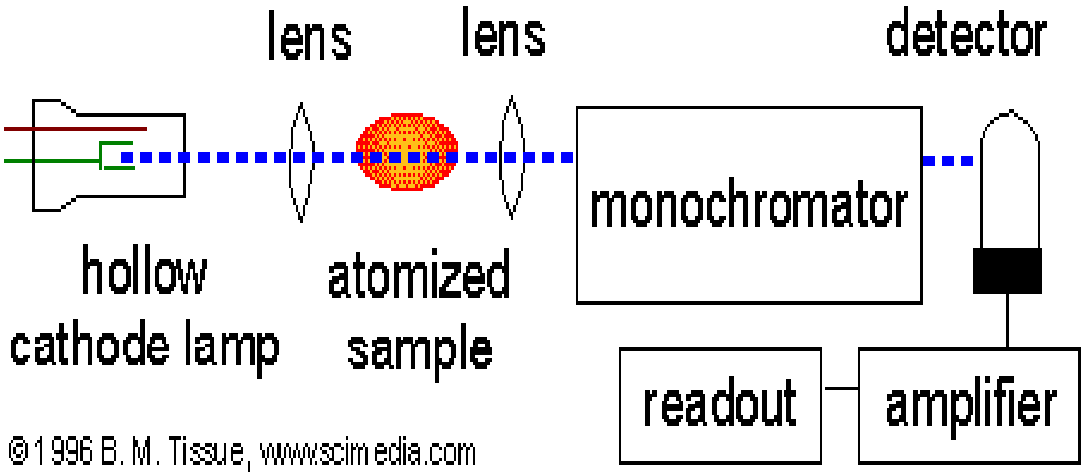

Figure 3.5 Schematic diagram of Varian AA240FS Atomic Absorption Spectrophotometer

3.5.1 Elemental analysis of grinding plate

Analysis of heavy metals of interest in the grinding plate was performed using a Varian AA240FS Atomic Absorption Spectrophotometer (APHA, 1989) with the recommended instrument parameters including detection limits for each metal determined (table 3.1). Blanks and standard reference materials were also run concurrently with the metal analyses to ensure reproducibly and quality assurance.

Final concentrations of metals were calculated from AAS readings by using the formula below:

$$C_T = \frac{C_m \text{ x } V}{M}$$

Where

C_T denotes final concentration of total metal

C_m denotes concentrations of analytes generated by the AAS

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V (Nominal volume) denote final volume of 30ml solution prepared

M denotes mass of the weighed sample for digestion.

3.5.2 Elemental analysis for Corn flour

The filtered samples were assayed for the presence of metals on a Varian AA240FS Atomic Absorption Spectrophotometer (APHA, 1989) with the recommended instrument parameters including detection limits for each metal determined (table 3.1). Blanks and standard reference reagents were also run concurrently with the metal analyses to ascertain reproducibly and quality assurance, at the Nuclear Chemistry and Environmental Research Centre (Instrumental Inorganic Laboratory), GAEC, Accra.

Final concentrations of metals were calculated from AAS readings by the formula below:

$$C_T = \frac{C_m \times V}{M}$$

Where

C_T denotes final concentration of total metal

Cm denotes concentrations of analytes generated by the AAS

V (Nominal volume) denote final volume of 30 ml solution prepared

M denotes mass of the weighed sample for digestion.

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Table 3.1 Operational Working Conditions (AAS)

ELEMENT	WAVELENGTH nm	LAMP CURRENT nA	SLIT WIDTH nm	DETECTION LIMIT mg/l	FUEL	SUPPORT
Zn	213.9	5	1.0	0.001	ACETYLENE	AIR
Ni	232.0	4	0.2	0.001	ACETYLENE	AIR
Fe	248.3	5	0.2	0.006	ACETYLENE	AIR
Mn	279.5	5	0.2	0.002		AIR
Cu	324.7	4	0.5	0.003		AIR
Cd	228.8	4	0.5	0.002	ACETYLENE	AIR
Pb	217.0	5	1.0	0.001	ACETYLENE	AIR
Cr	357.9	7	0.2	0.001	ACETYLENE	AIR
Co	240.7	7	0.2	0.005	ACETYLENE	NITROUS OXIDE
As(By Hydride)	193.7	10	0.5	0.001	ACETYLENE	NITROUS OXIDE
Hg(By Hydride)	253.7	4	0.5	0.001	ACETYLENE	AIR

Ref: VARIAN. Publication No 85- 100009-00 Revised March 1989.

Table 3.2 Weight recorded by grinding plate.

Specimen	Initial weight (kg)	Final weight (kg)	Weight Difference (Kg)
Ghana made Plate	5.3	4.6	0.7
India made plate	5.0	4.7	0.3
Nigeria made plate	5.1	4.6	0.5

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3.6 Human Health Risk Assessment (HHRA)

Health risk index (HRI)

The exposure pathway of heavy metals to human through ingestion of contaminated food has been studied by many researchers (Copat *et al.*, 2012; Xue *et al.*, 2012; Chary *et al.*, 2008). The estimated daily intake (EDI) of each heavy metal in this exposure pathway was determined by the equations below: Health risk of consumers due to intake of metal contaminated fish was assessed by using HRI. A HRI less than 1 means the exposed population is unlikely to experience obvious adverse effects; whereas a HRI above 1 means that there is a chance of non-carcinogenic effects, with an increasing probability as the value increases. The HRI was calculated by using the equation below (Wang *et al.*, 2005).

Health risk index (HRI)

- $HRI = \frac{EDI}{RfD}$, $EDI = \frac{Ef \times ED \times D \times Cm}{W \times Ef \times ED}$

EDI is estimated daily intake.

Rf D is Oral reference Dose (WHO, 2006)

Ef is exposure frequency (365days/year)

ED is exposure duration, equivalent to average life time (64years for Ghanaian)

D is food ingestion rate, which was considered to be 100g/person/day (Lanre and Adekule, 2012)

Cm is heavy metal concentration in milled maize (mg/kg)

W is average body weight (70kg)

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Where reference oral doses (RfD) for Cr, Cu, Zn, Fe, Ni, Pb, Mn and Cd are 1.5x 10-3, 4.0 x 10-2, 3.0 x 10-1, 7.0x 10-1, 2.0 x 10-2, 3.5 x 10-3, 3.3x10-2, 1.4 x 10-1 and 1.0 x 10-3 mg/kg/day respectively (USEPA, 2009).

It has been reported that exposure to two or more pollutants may result in additive and/or interactive effects. The total HRI of heavy metals for individual foodstuff was treated as the arithmetical sum of the individual metal HRI (Zheng *et al.*, 2007): Total HRI (individual foodstuff) = HRI (toxicant 1) + HRI (toxicant 2) + . . . HRI (toxicant n)

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CHAPTER FOUR

RESULTS AND DISCUSSION

The validity of the data generated in this study was checked using reference materials with known elemental concentrations. These were taken through the same process as did for the samples. The percentages recovery rate of the standard element detected were high and within acceptable limit, of 95% to 100.4% as shown in table 4.2. Samples were analysed in triplicates. The grinding plates from Ghana, India and Nigeria were analysed using atomic absorption spectrometer technique. The elemental concentrations of the grinding plates are shown in Table 4.1.

Table 4.1 Elemental concentration of the plates from Ghana, India and Nigeria (mg/kg)

	As	Pb	Cr	Mn	Co	Fe	Cu	Zn	Ni	Cd
Ghana	<0.01	0.210 ±0.15	12.200 ±0.01	6.30 ±0.31	0.300 ±0.02	325.155 ±1.80	12.700 ±0.12	5.300 ±0.91	20.920 ±1.40	0.240 ±0.32
India	<0.01	<0.01	10.200 ±0.03	5.000 ±0.22	0.130 ±0.12	155.700 ±1.50	10.500 ±0.13	0.93 ±0.60	9.160 ±1.00	<0.01
Nigeria	<0.01	0.180 ±0.17	3.100 ±0.05	5.510 ±0.41	0.200 ±0.05	205.050 ±1.83	5.980 ±0.11	0.94 ±0.55	15.300 ±1.30	0.220 ±0.22

Table 4. 2 Recovery rate for the selected heavy metals as determined with quality control standard

STD-QC	Fe	Zn	Mn	Cd	Pb	Co	Ni	Cu	Cr	As
%Recovery	99.9	97.6	95.0	99.7	100.0	99.5	99.8	100.0	100.0	100.0

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Table 4.3: National Research Council recommended daily dietary iron allowances (1989)

Age group	Age(yrs)	Iron (mg)
Infants	-0.5	10
	0.5-1.0	15
	1-3	15
	4-6	10
Children	7-10	10
	11-14	18
	15-18	18
	19-22	10
Male	23-50	10
	50+	10
		18
Female	11-14	18
	15-18	18
	19-22	18
	23-50	10
	50+	

Comparing the recorded concentration values from the three different grinding plates, it can be observed that Ghanaian plate showed significant Zn concentration levels. Fe, Ni, Cu and Cr are present in significant levels in all the three different plates.

The composition of the grinding plates could affect the concentration of the metals in the milled maize flour. The Ghanaian, Indian and Nigerian made grinding plate were used for grinding in three different milling machines at Dome Market in Accra. Generally, the concentrations of the metals in the corn flour obtained from the milling process was highest in Ghanaian made plate followed by that of Nigerian made plate with the Indian made plate having the relatively lower levels. This indicates that the

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India made plate can be comparatively considered to be of a better quality.

The metal concentrations in the original maize was found to be lower than that obtained from the three grinding plates

The elemental concentrations of the milled maize samples using the Ghanaian, Indian and Nigerian made grinding plates are shown in figures 4.1 to 4.9.

Cadmium

The results of cadmium content in the grinding plates, original maize and the corn flour obtained from the milled maize have been presented in Fig 4.1. The concentration of Cd in the original maize flour is 0.02 mg/kg. The Cd concentration recorded in all the milled maize flours were higher than that obtained in the original maize. This shows that the milling process introduced some amount of the Cd metal into the maize flour during the milling process. Cadmium (Cd) recorded a concentration value of 0.21 mg/kg, 0.1 mg/kg, 0.07 mg/kg and 0.02 mg/kg at the first; second, third and fourth milling respectively using the Ghanaian made plate. The Cd concentration shows decreases trend from the first month (first milling) to the fourth month (fourth milling). Similar trend can also be seen with the Nigerian plate although it recorded relatively lower values than that with the Ghanaian made plate. The Cd concentration from that with the Indian plate maintained the same value of 0.02 mg/kg in the four. The observed trend of lower concentrations recorded with time shows that the rate of wear decreases with time as the plates are being used. The rate of wear can be said to vary for the three different plates.

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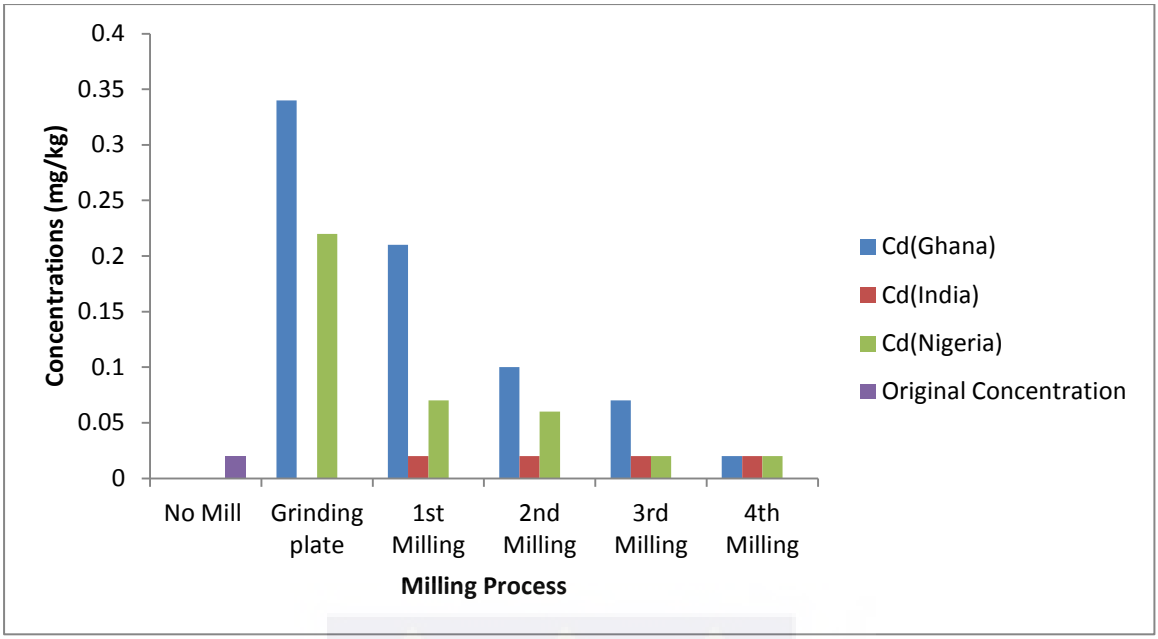

Figure 4.1 Concentration of Cd in the milled corn- flour

Generally, the concentrations of Cd in the milled maize samples from all the three grinding plates Ghanaian (0.02 – 0.1 mg/kg), Indian (0.02 mg/kg) and Nigerian (0.02 – 0.07 mg/kg) made plates are below WHO standard and also the EC regulation for Cd in food (0.2 mg/kg). Kikuchi et al. (2002) and Frazzoli et al. (2007) had cadmium concentrations in corn flour samples from 0.004 to 0.38 and 0.005 to 0.49 mg/kg, respectively for the two different works.

The exceeding levels of cadmium can affect human health. Cadmium can disturb kidney functions, and some studies indicate a cancerous effect. Research has proved that, those countries whose main food is cereals, the consumption of these cereals causes an intake of cadmium. Machiwa, 2010 had reported that 50% of cadmium intake comes from the cereal consumption and in Japan this amount was 40 to 60%. The Asian Governments have established critical maximum levels of heavy metals in cereals to protect the health of their citizens. In Japan the maximum level of cadmium

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in unpolished cereal is 1.0 mg/kg while in China the maximum permitted level is 0.4 mg/kg of polished cereals (Chen, 2000).

European Union (EU) food legislation provides an overview of maximum permissible level of cadmium concentration in cereal is 0.2 mg/kg (EU, 2006).

Lead

The results pertaining to the lead in the grinding plates, the original maize and the corn flour obtained from the milled maize have been presented in Fig 4.2. The concentration value of Pb in the original maize is 0.02 mg/kg. The Pb concentration recorded in all the milled maize flours were higher than that obtained in the original maize. This shows that the milling process introduced some amount of the Pb metal into the maize flour.

The Pb concentration in the milled maize flour using the Ghanaian and Nigerian plates similarly followed a decreasing trend with time of the milling process. Similarly as in the case of Pb, 0.02 mg/kg Pb concentration was maintained in all the four millings with the Indian plate

Considering the rate of decreasing Pb contents at the different times of the milling, it can be seen that the rate of wear varied with the three different plates.

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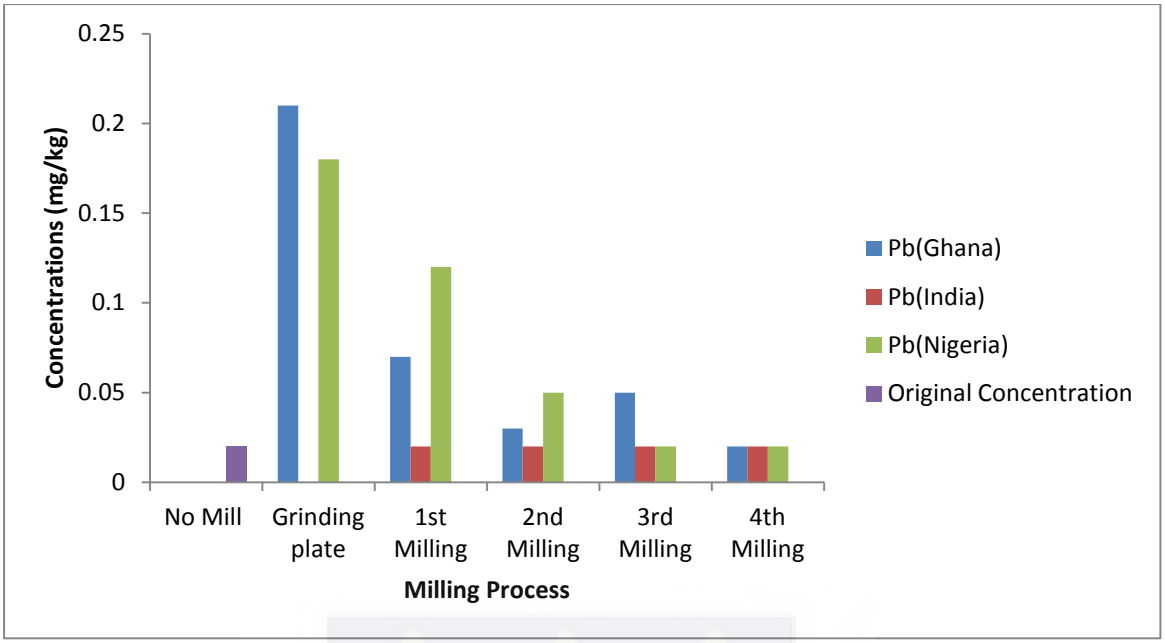

Figure 4.2 Concentration of Pb in the milled corn-flour

From table 4.8 the concentration of the Pb ranges between 0.02-0.07 mg/kg, 0.02-0.02 mg/kg, and 0.02-12 mg/kg for Ghanaian, Indian and Nigerian made plate respectively. Generally, the Pb concentrations in all the three plates are below WHO standard and the EC regulation for Pb in food both of which are 0.2 mg/kg. Lead was detected but at lower amounts, these amounts were relatively higher compared to those reported by other studies in Africa. Wyasu et al, (2010) in Nigeria reported 0.013 mg/kg).

The results of the present study are much lower than the results of Lin (1991) and Bakhtiarian (2001) who found higher lead concentrations of 0.43 and 0.74 mg/kg, respectively in cereals. Higher concentration of lead may cause brain complications; coma and death may occur if not treated instantly (EPA, 2013).

Copper

The results of the copper concentrations in grinding plates, the original maize, and the corn flour obtained from the milled maize have been presented in Fig 4.3. The concentration value of Cu in the original maize is 8.46 mg/kg. The Cu concentration recorded in all the milled maize flours were higher than that obtained in the original

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maize. This shows that the milling process introduced some amount of the Cu metal into the maize flour.

The Cu contents in the flour obtained from the Ghanaian made grinding plates recorded the highest concentrations of 10.21 - 15.02 mg/kg and that of India recording the least of 9.13 - 11.25 mg/kg. It can be seen from Fig 4.3 that the concentration followed a decreasing trend with the milling time.

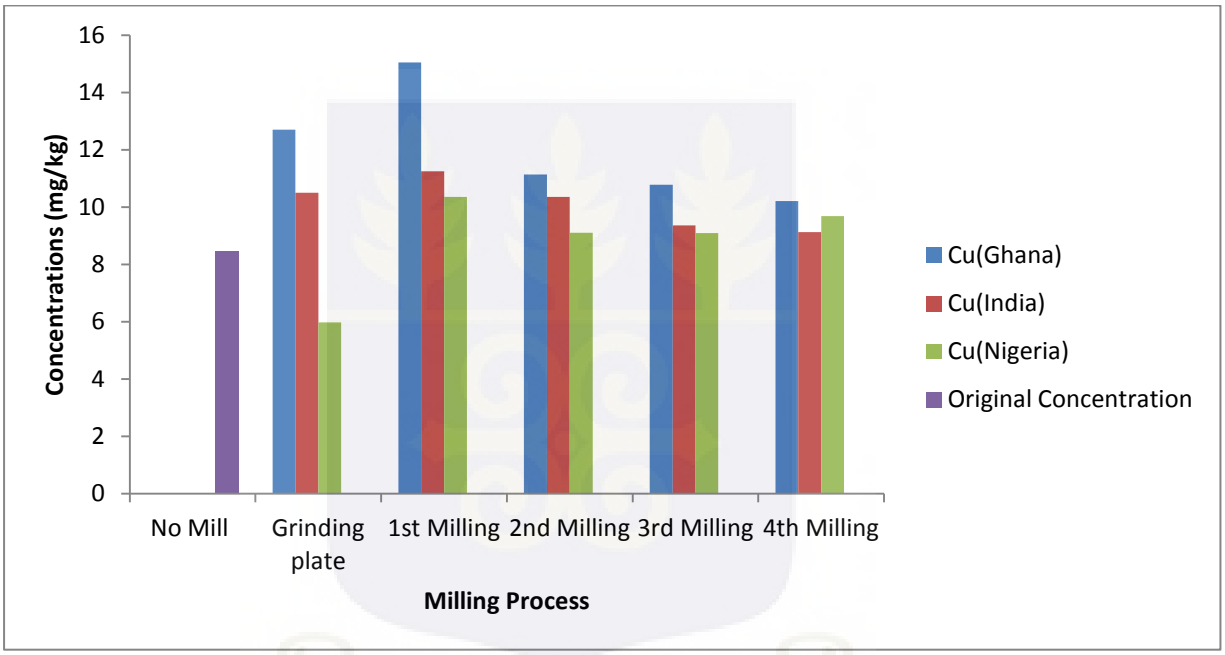

Figure 4.3 Concentration of Cu in the milled corn flour

. The Cu level of 10 mg/kg is acceptable by FAO/WHO, 2001, which is higher than the Cu level in the original maize. The Cu contents in the flour from the Ghanaian made plate (10.21 – 15.04 mg/kg) were higher than 10 mg/kg for the four milling process. The first milling stage with the Nigerian plates (10.36 mg/kg) and Indian made plates had level higher than 10 mg/kg. Abrefah et al, 2011 in Ghana reported a relatively lower value of 1.5 mg/kg.

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Nickel

Nickel concentrations in the grinding plates, in the maize and the corn flour obtained from the milled maize are presented in Fig 4.4. The Ni concentration in the original maize is 9.6 mg/kg. The Ni concentration recorded in all the milled maize flours were significantly higher than that obtained in the original maize with that of Ghanaian recording the highest values between 10.43 - 23.23 mg/kg. This shows that the milling process introduced some amount of the Ni metal into the maize flour.

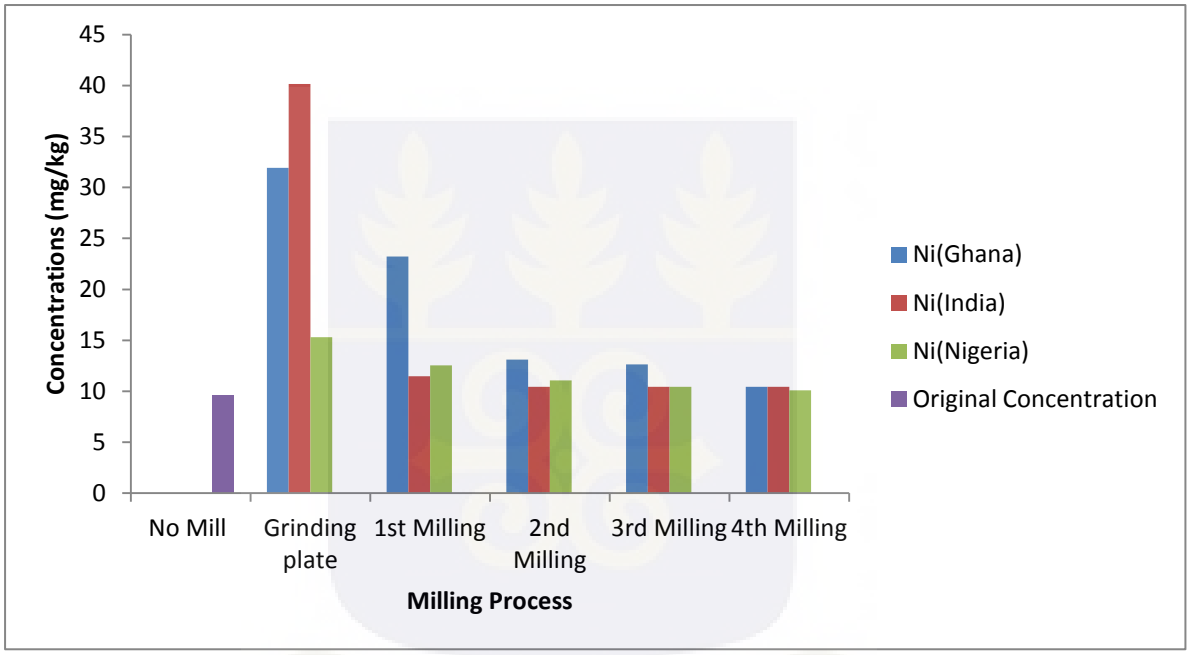

Figure 4.4 Concentration of Ni in the milled corn flour

From table 4.11 the Ni concentration ranges between 10.43 - 11.46 mg/kg and 10.09 - 12.55 mg/kg respectively for Indian and Nigerian made plates.

Generally, the concentrations of Ni in all the three plates are above level of 10 mg/kg proposed by FAO/WHO, 2001. The Ni content in the original maize was within the acceptable limits proposed by FAO/WHO. The Ni contents in all the milled maize were above the acceptable limits of 10 mg/kg. Work by Abrefah et al, 2011 in Ghana reported 26.18 mg/kg in corn flour.

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Higher concentration of nickel causes serious harmful health effects, such as chronic bronchitis, reduced lung function, and cancer of the lung and nasal sinus (USEPA, 2013).

Chromium

The results pertaining to the chromium original content in maize, grinding plates and the corn flour obtained from the milled maize have been presented in Fig 4.5. The original concentration value of Cr in the maize flour is 0.53 mg/kg. The Cr concentration recorded in all the milled maize flours exceeded that obtained in the original maize. This shows that the milling process introduced some amount of the Cr metal into the maize flour. Flour from the first millings with the three plates recorded significantly high contamination of Cr. The contamination deceased from the other subsequent millings.

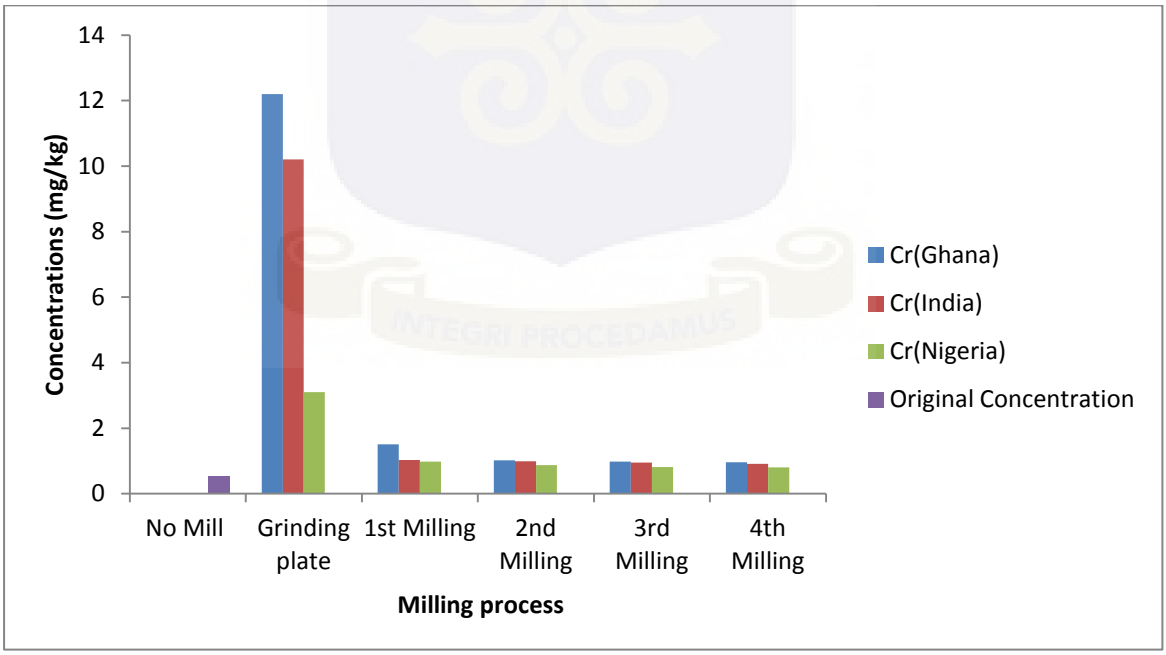

Figure 4.5 Concentration of Cr in the milled corn flour

From table 4.9, Cr concentration ranges between 0.96 - 1.51 mg/kg, 0.91- 1.03 mg/kg and 0.8 - 0.98 mg/kg respectively for Ghanaian-, Indian and Nigerian made plate.

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Generally, the concentration of Cr in maize flour with all the three plates are below level of 1.3 mg/kg proposed by FAO/WHO, 2001. Except first milling with Ghanaian made plate (1.51 mg/kg). Abrefah et al, 2011 recorded Cr levels below detection limit.

Too much chromium can also damage the liver, kidneys, and nerves, and it may cause irregular heart rhythm.

Cobalt

The cobalt contents in the grinding plates, the maize, and the corn flour obtained from the milled maize are presented in Fig 4.6. The concentration of Co in the original maize flour is 3.16 mg/kg. The Co concentration recorded in all the milled maize flours were higher than that obtained in the original maize but did not show much significant difference. The highest of 3.41 mg/kg was found in corn flour processed from Ghanaian made plate. This shows that the milling process introduced some amount of the Co metal into the maize flour.

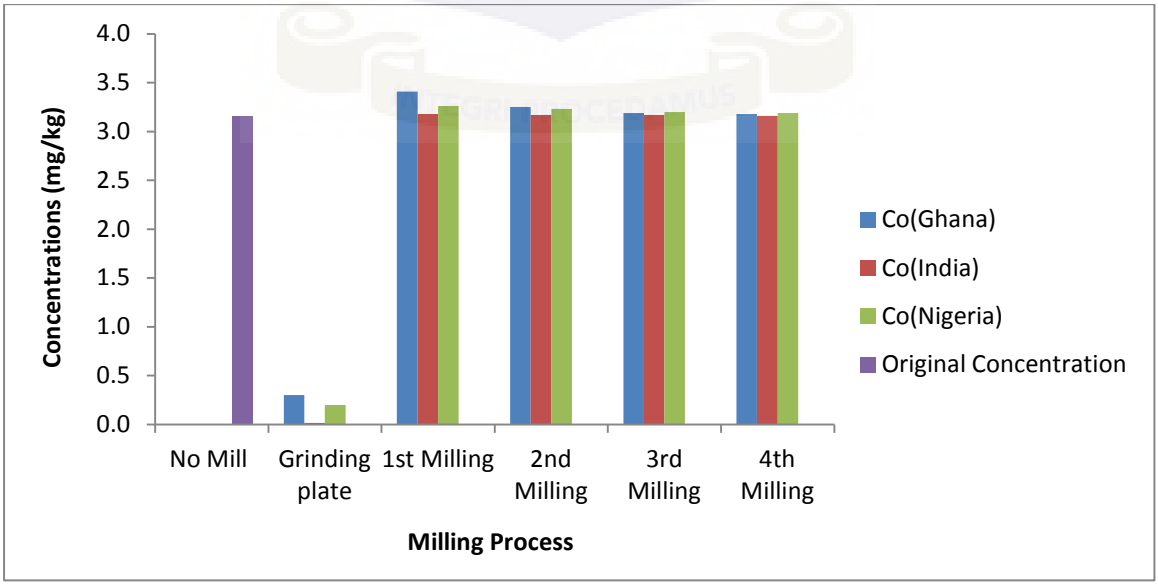

Figure 4.6 Concentration of Co in the milled corn flour

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Generally, the concentrations of Co in all the three plates are within level of 50 mg/kg proposed by FAO/WHO, 2001. Abrefah et al, 2011 recorded Co levels below detection limit.

Cobalt is beneficial to man, it stimulates the production of red blood cells, thus, used to treat anemia. However, too high concentration of the metal may have an ill-health effect

Manganese

The concentration of Mn in the grinding plates, the maize, and the corn flour obtained from the milled maize can be seen in Fig 4.7. The original concentration of Mn in the maize flour is 2.3 mg/kg. The Mn concentration recorded in all the milled maize flours were higher than that obtained in the original maize but of little significant difference. Similarly, the highest level of 5.83 mg/kg was recorded in the maize flour processed from the Ghanaian made plates. This shows that the milling process introduced some amount of the Mn metal into the maize flour.

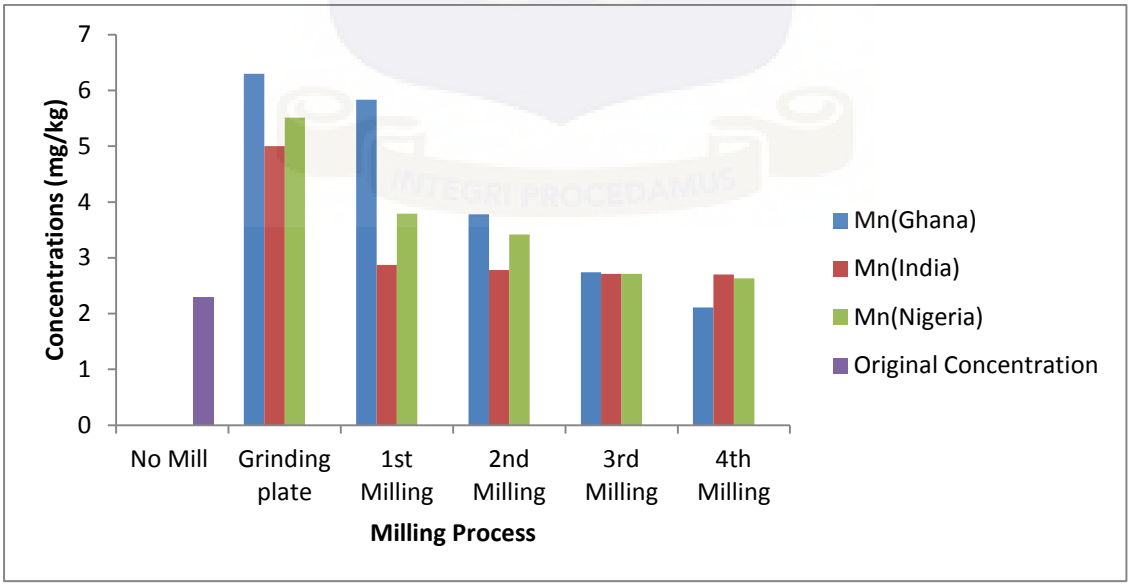

Figure 4.7 Concentration of Mn in the milled corn flour

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Generally, the concentration of Mn in the maize flour processed from all the three plates ,Ghanaian made plate (2.11 – 5.83) Indian made plate (2.7 – 2.87) and Nigerian made plate (2.63 – 3.79), were above 2.3 mg/kg proposed by FAO/WHO, 2001. Reported by other studies on corn flour have given the following, Ghanaian; 3.55 mg/kg, Turkey; 2.90 mg/kg, Pakistan; 20.2 mg/kg (Shar et al, 2002).

Zinc

The results of the zinc content in the grinding plates, the maize, and the corn flour obtained from the milled maize are presented in Fig 4.8. The Zn contents in the original maize are 16.88 mg/kg. The Zn concentration recorded in all the milled maize flours were higher than that obtained in the original maize. The milling process can be said to have introduced some amount of the Zn metal into the maize flour. The Zn contamination was more significant with the Ghanaian made grinding plate (17.21 - 30.97 mg/kg) with the least from the Indian made plate (16.95 - 17.99 mg/kg). The Nigerian made plate recorded concentration of 17.59 - 20.48 mg/kg. The Zn concentrations is also seen to decrease with time as the plates are being used for all the three plates but that of Ghanaian showed much significant variations.

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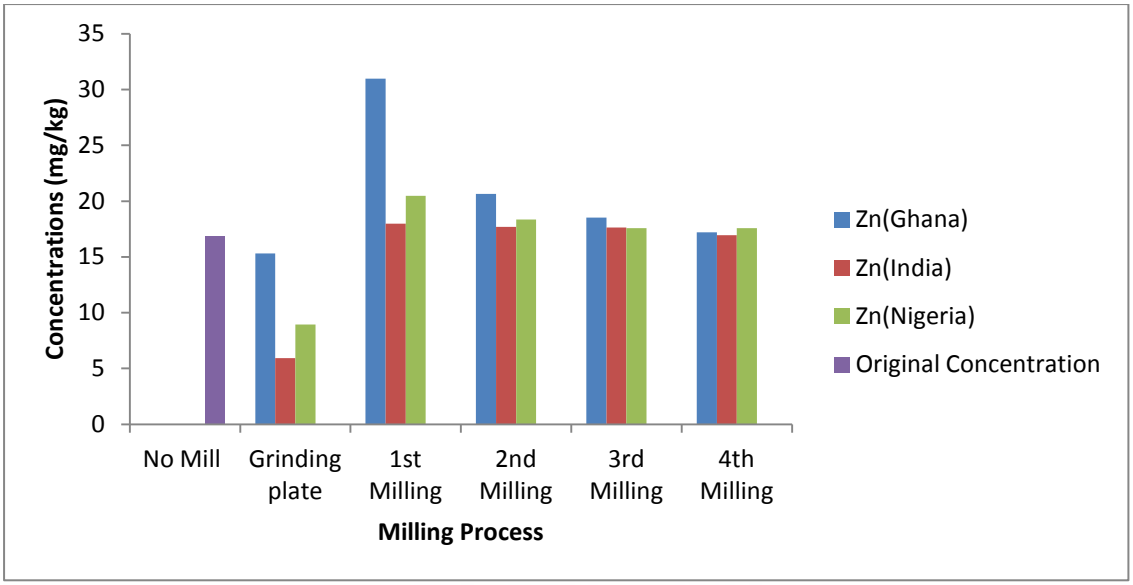

Figure 4.8 concentrations Zn in the milled corn flour

Generally, the concentrations of Zn in the maize flour processed from all the three plates are within level of 50 mg/kg proposed by FAO/WHO, 2001. Other works have reported Zn concentrations in corn flour as follows: flour made in Ethiopia, (between 6.00 mg/kg and 9.90 mg/kg); USA, (between 7.0 mg/kg and 7.2 mg/kg); Romania, (13.97 mg/kg, and Nigeria, (0.019 mg/kg and 2.93 mg/kg) (Cuadrado et al, 2000)..

Iron

The results pertaining to the original content of iron in maize, grinding plates and the corn flour obtained from the milled maize can be seen in Fig 4.9. The original concentration value of Fe in the maize flour is 32.1 mg/kg. The Fe concentration recorded in all the milled maize flours were much higher than that obtained in the original maize. This shows that the milling process introduced some amount of the Fe metal into the maize flour. The high difference between Fe content in the original maize and that of the maize flour from the grinding plates can be due to the fact that Fe form the highest percentage concentration of the alloy used for the grinding plate

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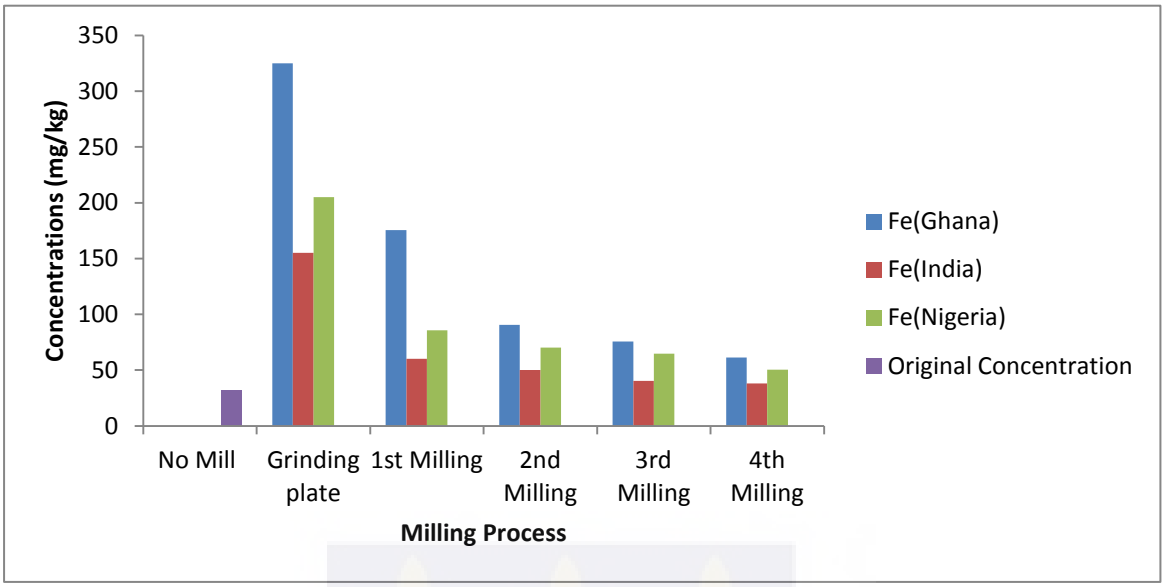

Figure 4.9 Elemental concentration of Fe in the milled corn flour

From table 4.6, Fe recorded a concentration ranging between 61.24 - 175.34 mg/kg, 38.08 - 60.11 mg/kg and 50.57 - 85.78 mg/kg respectively for Ghanaian-, Indian- and Nigerian made plate. Generally, the concentrations of Fe in all the three plates are within level of 425.5 mg/kg proposed by FAO/WHO, 2001. The amount detected was relatively higher compared to those reported by Kwofie et al, 2011 for corn flour in Ghana (0.05 mg/kg). Iron is an essential element in humans as it helps in oxygen transport and also regulates cell growth and differentiation (Andrews, 1999). Deficency of iron will therefore limits oxygen delivery to cells resulting in fatigue, poor work performance, and decrease immunity (Bhaskaram, 2001; Haas and Brownnlie, 201l) Nevertheless, excess iron intake can result in iron overload and toxicity, arrhythmia, heart farewilure, increased atherosclerosis risk, and increases in the risk of liver, breast, gastrointestinal, and hematologic cancers (Araujo et al, 1995; Nelson et al, 1995; Sahinbegovic et al, 2010; Ellervik et al, 2012; Kallianpur et al, 2004; Dongiovanni et al, 2011; Kremastinos et al, 2011).

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Health Risk Assessment

The average estimated daily intake, (EDI) of heavy metals in milled maize consumption is given in Table 2. The first milling had relatively high EDI values greater than the subsequent ones for all the three grinding plates. The mean EDI values of the individual heavy metals in the milled maize were below their corresponding oral reference dose (RfD) values recommended by USEPA, 2009. The RfD represents an estimation of the daily exposure of a contaminant to which the human population may be continually exposed over a lifetime without an appreciable risk of harmful effects. Even though the concentration of Ni, Cr and Cu found in the milled maize for the first milling were above the limit set by European regulation, the subsequent ones did not show levels that could pose a risk to human health since the EDIs calculated for these metals were below the RfD values.

Result of health risk assessments (HRI) of the various heavy metals considered in this study is presented in Table 4.4. The results indicate that Cu, Cr and Ni have HRI value > 1 within the first month of grinding; indicating that human's would experience health risk if they only consume metals from milled maize from Ghana made plate within the first month of grinding. Among the heavy metals examined in this study, Ni with a HRI value of 1.63 using the Ghana made plate, would have a relatively higher potential health risk, whiles Pb (HRI= $8.16x10^{-3}$) has the lowest potential health risk.

Reports have it that exposure to more than one contaminant may produce an additive effect on the organism. In this study, the total HRIs of the individual metals examined in the milled maize samples was calculated by adding the individual HRIs of the metals. The total HRI through the consumption of milled maize after the first month of continuous use of the plates was less than 1, indicating that there is no potential

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significant health risk associated with the consumption of milled maize after the first month. Ni and Cr were the elements found to pose significant human health risk in the study.

Table 4.4 EDI and HRI concentrations in milled maize

Heavy metal	RfD	Ghana made plate		India made plate		Nigeria made plate	
		EDI	HRI	EDI	HRI	EDI	HRI
Fe	$7.0x10^{-1}$						
1st milling		2.50×10^{-1}	3.58×10^{-1}	8.59×10^{-1}	1.23×10^{-1}	1.23×10^{-1}	1.75×10^{-1}
2nd milling		1.29 x 10-1	1.85×10^{-1}	7.12×10^{-1}	1.02×10^{-1}	1.00×10^{-1}	1.43×10^{-1}
3rd milling		1.08 x10-1	1.54×10^{-1}	5.78×10^{-1}	8.26×10^{-1}	9.27×10^{-1}	1.32×10^{-1}
4th milling		8.75 x10-2	1.25×10^{-1}	5.44×10^{-1}	7.78×10^{-1}	7.22×10^{-1}	1.03×10^{-1}
Cu	$4.0x10^{-2}$						
1st milling		$2.15x\ 10^{-2}$	1.54×10^{-2}	1.61×10^{-2}	4.02×10^{-1}	1.48×10^{-2}	3.70×10^{-1}
2nd milling		5.37×10^{-1}	3.85×10^{-1}	1.48×10^{-2}	3.70×10^{-1}	1.30×10^{-2}	3.25×10^{-1}
3rd milling		1.59×10^{-2}	1.46×10^{-2}	1.34×10^{-2}	3.33×10^{-1}	1.30×10^{-2}	3.25×10^{-1}
4th milling		3.98×10^{-1}	2.08×10^{-1}	1.30×10^{-2}	3.26×10^{-1}	1.38×10^{-2}	3.46×10^{-1}
Zn	$3.0x10^{-1}$						
1st milling		4.42×10^{-2}	1.47×10^{-1}	2.96×10^{-2}	9.85×10^{-2}	3.35×10^{-2}	1.12×10^{-1}
2nd milling		3.52×10^{-2}	1.17×10^{-2}	2.84×10^{-2}	9.47×10^{-2}	2.76×10^{-2}	9.21×10^{-2}
3rd milling		2.79×10^{-2}	9.30×10^{-2}	2.75×10^{-2}	9.16×10^{-2}	2.37×10^{-2}	7.89×10^{-2}
4th milling		2.32×10^{-2}	7.72×10^{-2}	2.70×10^{-2}	9.02×10^{-2}	2.23×10^{-2}	7.42×10^{-2}

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Co	$3.0x10^{-1}$						
1st milling		$4.0x10^{-4}$	$5.71x10^{-4}$	$2.5x10^{-4}$	$3.67x10^{-4}$	$3.71x10^{-4}$	$5.31x10^{-4}$
2nd milling		$3.57x10^{-4}$	$5.10x10^{-4}$	$2.4x10^{-4}$	$3.47x10^{-4}$	$3.29x10^{-4}$	$4.69x10^{-4}$
3rd milling		$2.71x10^{-4}$	$3.88x10^{-4}$	$2.42x10^{-4}$	$3.47x10^{-4}$	$2.86x10^{-4}$	$4.08x10^{-4}$
4th milling		$2.57x10^{-4}$	$3.67x10^{-4}$	$2.23x10^{-4}$	$3.27x10^{-4}$	$2.71x10^{-4}$	$3.88x10^{-4}$
Pb	$3.5x10^{-3}$						
1st milling		$1.0x10^{-4}$	$2.86x10^{-2}$	$2.86x10^{-5}$	$8.16x10^{-3}$	$1.71x10^{-4}$	$4.90x10^{-2}$
2nd milling		$4.28x10^{-5}$	$1.22x10^{-2}$	$2.86x10^{-5}$	$8.16x10^{-3}$	$7.14x10^{-5}$	$2.04x10^{-2}$
3rd milling		$7.14x10^{-5}$	$2.04x10^{-2}$	$2.86x10^{-5}$	$8.16x10^{-3}$	$2.86x10^{-5}$	$8.16x10^{-3}$
4th milling		$2.86x10^{-5}$	$8.16x10^{-3}$	$2.86x10^{-5}$	$8.16x10^{-3}$	$2.86x10^{-5}$	$8.16x10^{-3}$
Cd	$1.4x10^{-1}$						
1st milling		$3.0x10^{-4}$	$4.08x10^{-4}$	$2.86x10^{-5}$	$2.04x10^{-4}$	$1.0x10^{-4}$	$7.14x10^{-4}$
2nd milling		$1.43x10^{-4}$	$1.02x10^{-3}$	$2.86x10^{-5}$	$2.04x10^{-4}$	$8.37x10^{-5}$	$6.12x10^{-4}$
3rd milling		$1.0x10^{-4}$	$7.14x10^{-4}$	$2.86x10^{-5}$	$2.04x10^{-4}$	$2.86x10^{-5}$	$2.04x10^{-4}$
4th milling		$2.86x10^{-5}$	$2.04x10^{-4}$	$2.86x10^{-5}$	$2.04x10^{-4}$	$2.86x10^{-5}$	$2.04x10^{-4}$
Ni	$2.0x10^{-2}$						
1st milling		$3.32x10^{-2}$	$1.65x10^{0}$	$1.64x10^{-2}$	$8.19x10^{-1}$	$1.79x10^{-2}$	$8.96x10^{-1}$
2nd milling		$1.87x10^{-2}$	$9.40x10^{-1}$	$1.49x10^{-2}$	$7.46x10^{-1}$	$1.58x10^{-2}$	$7.89x10^{-1}$
3rd milling		$1.80x10^{-2}$	$9.01x10^{-1}$	$1.49x10^{-2}$	$7.46x10^{-1}$	$1.49x10^{-3}$	$7.45x10^{-1}$
4th milling		$1.49x10^{-2}$	$7.45x10^{-1}$	$1.49x10^{-2}$	$7.46x10^{-1}$	$1.44x10^{-3}$	$7.21x10^{-1}$
Cr	$1.5x10^{-3}$						
1st milling		$2.57x10^{-3}$	$1.438x10^{0}$	$1.47x10^{-3}$	$9.81x10^{-1}$	$1.40x10^{-3}$	$9.33x10^{-1}$
2nd milling		$1.46x10^{-3}$	$9.71x10^{-1}$	$1.41x10^{-3}$	$9.43x10^{-1}$	$1.24x10^{-3}$	$8.29x10^{-1}$
3rd milling		$1.40x10^{-3}$	$9.33x10^{-1}$	$1.36x10^{-3}$	$9.04x10^{-1}$	$1.16x10^{-3}$	$7.71x10^{-1}$
4th milling		$1.37x10^{-3}$	$9.10x10^{-1}$	$1.30x10^{-3}$	$8.67x10^{-1}$	$1.14x10^{-3}$	$7.62x10^{-1}$
Mn	$3.3x10^{-2}$						
1st milling		$8.33x10^{-3}$	$2.52x10^{-1}$	$4.10x10^{-3}$	$1.24x10^{-1}$	$5.41x10^{-3}$	$1.64x10^{-1}$

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2nd milling		$8.26x10^{-3}$	$2.50x10^{-1}$	$3.97x10^{-3}$	$1.20x10^{-1}$	$4.89x10^{-3}$	$1.48x10^{-1}$
3rd milling		$6.77x\ 10^{-1}$	$2.05x10^{-1}$	$3.87x10^{-3}$	$1.17x10^{-1}$	$3.87x10^{-3}$	$1.17x10^{-1}$
4th milling		$6.73x10^{-3}$	$2.04x10^{-1}$	$3.86x10^{-3}$	$1.17x10^{-1}$	$3.76x10^{-3}$	$1.14x10^{-1}$

Table 4.5 Concentrations of Cobalt

Column1	Co(Ghana)	Co(India)	Co(Nigeria)	Original Concentration
No Mill				3.16
Grinding plate	0.3	0.015	0.2	
1st Milling	3.41	3.18	3.26	
2nd Milling	3.25	3.17	3.23	
3rd Milling	3.19	3.17	3.2	
4th Milling	3.18	3.16	3.19	

Table 4.6 Concentrations of Zinc

Column1	Zn(Ghana)	Zn(India)	Zn(Nigeria)	Original Concentration
No Mill				16.88
Grinding plate	15.3	5.93	8.94	
1st Milling	30.97	17.99	20.48	
2nd Milling	20.64	17.69	18.35	
3rd Milling	18.52	17.63	17.57	
4th Milling	17.21	16.95	17.59	

Table 4.7 Concentrations of Iron

Column1	Fe(Ghana)	Fe(India)	Fe(Nigeria)	Original Concentration
No Mill				32.1
Grinding plate	325	155	205	
1st Milling	175.34	60.11	85.78	
2nd Milling	90.62	50.21	70.23	
3rd Milling	75.56	40.48	64.89	
4th Milling	61.24	38.08	50.57	

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Table 4.8 Concentrations of Cadmium

Column1	Cd(Ghana)	Cd(India)	Cd(Nigeria)	Original Concentration
No Mill				0.02
Grinding plate	0.34	<0.01	0.22	
1st Milling	0.21	0.02	0.07	
2nd Milling	0.1	0.02	0.06	
3rd Milling	0.07	0.02	0.02	
4th Milling	0.02	0.02	0.02	

Table 4.9 Concentrations of Lead

Column1	Pb(Ghana)	Pb(India)	Pb(Nigeria)	Original Concentration
No Mill				0.02
Grinding plate	0.21	<0.01	0.18	
1st Milling	0.07	0.02	0.12	
2nd Milling	0.03	0.02	0.05	
3rd Milling	0.05	0.02	0.02	
4th Milling	0.02	0.02	0.02	

Table 4.10 Concentrations of Chromium

Column1	Cr(Ghana)	Cr(India)	Cr(Nigeria)	Original Concentration
No Mill				0.53
Grinding plate	12.2	10.2	3.1	
1st Milling	1.51	1.03	0.98	
2nd Milling	1.02	0.99	0.87	
3rd Milling	0.98	0.95	0.81	
4th Milling	0.96	0.91	0.8	

Table 4.11 Concentrations of Manganese

	Mn(Ghana)	Mn(India)	Mn(Nigeria)	Original Concentration
No Mill				2.3
Grinding plate	6.3	5	5.51	
1st Milling	5.83	2.87	3.79	
2nd Milling	3.78	2.78	3.42	
3rd Milling	2.74	2.71	2.71	
4th Milling	2.11	2.7	2.63	

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Table 4.12 Concentrations of Nickel

Column1	Ni(Ghana)	Ni(India)	Ni(Nigeria)	Original Concentration
No Mill				9.6
Grinding plate	31.92	40.16	15.3	
1st Milling	23.23	11.46	12.55	
2nd Milling	13.12	10.44	11.05	
3rd Milling	12.62	10.43	10.43	
4th Milling	10.43	10.43	10.09	

Table 4.13 Concentrations of Copper

Column1	Cu(Ghana)	Cu(India)	Cu(Nigeria)	Original Concentration
No Mill				8.46
Grinding plate	12.7	10.5	5.98	
1st Milling	15.04	11.25	10.36	
2nd Milling	11.14	10.35	9.11	
3rd Milling	10.78	9.36	9.09	
4th Milling	10.21	9.13	9.68	

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CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

The results recorded indicated that the heavy metals (Cd, Pb, Cu, Ni, Cr, Mn, Co, Zn, Fe and As) content of the Ghana, India and Nigeria made plates had the similar elements but varied in terms of the individual metal concentrations. The Ghanaian made plate was found to wear faster relative to Nigerian and Indian made plate. The Ghana made plates was found to cause more contamination than the other two but generally, the India made plates caused least contamination.

The India made plates had the least Cd and Pb concentration levels. The elemental concentration and the risk assessment calculations have shown that contamination of milled products are highest within the first month of the use of the grinding plates but can decreases considerably with time.

The HRI value for first milled maize with locally made grinding plate showed human health problem for Cr and Ni metals contaminations in the maize flour.

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5.2 RECOMMENDATIONS

I recommend that

- Using newly sharpened grinding plate, about 2 kg of maize should be grinded and discarded before grinding for household consumption.
- Ghanaian made plates should be well branded as it is done for the foreign ones to help trace the source of manufacture.
- There should be an improvement in the hardness and metal contents of the Ghanaian made plates to prevent the high contamination of metals in milled products.
- The manufacturers of grinding plates should be well monitored to ensure that their product meets the required quality.
- Ghana should set standard for grinding plates for manufactures to follow the standard production procedures to ensure quality products.

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REFERENCES

Abelsohn AR, Sanborn M (2010). Lead and children: clinical management for family physicians. Can Fam Physician. 56(6):531-5

Abrefah et al./ Elixir Agriculture 39 (2011) 5000-5003

Adal A, Wiener SW (2013). Medscape. Heavy Metal Toxicity. http://emedicine.medscape.com/article/814960-overview. Accessed 10/8/2013.

Afal A& Wiener SW (2014), Metal Toxic Medscape.org, viewed 21 April 20143/2006, Institute of Nuclear Chemistry and Technology, Warsaw, Poland (2006).

Aguilera, Jose Miguel and David W. Stanley (1999). *Microstructural Principles of Food Processing and Engineering*. Springer. ISBN 0-8342-1256-0.

Andrews, N. C. (1999) "Disorders of iron me-tabolism", *N Engl J Med, 34: 1986-95*.

Araujo JA, Romano EL, Brito BE, Parthé V, Romano M, Bracho M, Montaño RF, Cardier J (1995). Iron overload augments the development of atherosclerotic lesions in rabbits. Arterioscler Thromb Vasc Biol. 15(8):1172-80

Arita A, Costa M (2009). Epigenetics in metal carcinogenesis: nickel, arsenic, chromium and cadmium. *Metallomics : integrated biometal science.* 1(3):222-228.

ASTM International (2006) ASTM C 738-94, "Standard Test Method for Lead and Cadmium Extracted from Glazed Ceramic Surfaces".

Anzelmo, John A. and Lindsay, James R. (1987). *Journal of Chemical Education*, 64(9). A200-A204.

Atiemo, S. M., Ofosu, F. G., Aboh, I. J. K., Yeboah, P. E., (2010). Determination of heavy metals and human risk assessment of road dust on the Tema Motorway and Tetteh Quasrshie Interchange in Accra, Ghana.

ATSDR. Toxicological Profile For Aluminum (2008b) 1–357. Available online at http://www.atsdr.cdc.gov/toxprofiles/tp22.pdf1983.

ATSDR.Case Studies in Environmental Medicine (2004) 1–42. Available online at http://www.atsdr.cdc.gov/csem/arsenic/docs/arsenic.pdf

ATSDR.Detailed Data Table for the (2011) Priority List of Hazardous Substances 2011: 1–20. Available online at http://www.atsdr.cdc.gov/spl/resources/ATSDR_2011_SPL_Detailed_Data_Table.pdf

ATSDR.Mercury ToxFAQ. (2000) 1–2. Available online at http://www.atsdr.cdc.gov/toxfaqs/tfacts46_metallic_mercury.pdf

University of Ghana http://ugspace.ug.edu.gh

ATSDR.ToxGuide for Cadmium. 2012a:1–2. Available online at www.atsdr.cdc.gov/toxguides/toxguide-5.pdf

ATSDR.ToxGuide for Lead. 2008a:1–2. Available online at http://www.atsdr.cdc.gov/toxguides/toxguide-13.pdf

ATSDR.Toxicological Profile for Arsenic. 2007a:1–559. Available online at http://www.atsdr.cdc.gov/toxprofiles/tp2.pdf

ATSDR.Toxicological Profile for Cadmium. 2012b:1–487. Available online at http://www.atsdr.cdc.gov/toxprofiles/tp5.pdf

ATSDR.Toxicological Profile for Lead. 2007b; 1–582. Available online at http://www.atsdr.cdc.gov/toxprofiles/tp13.pdf

ATSDR.Toxicological Profile for Mercury.2001; 1–676. Available online at http://www.atsdr.cdc.gov/toxprofiles/tp46.pdf

Bakhtiarian A, Gholipour V and Ghazi-Khansar M (2001). Lead and Cadmium Content of Korbal Rice in Northern Iran, Iranian J. Publ. Health, 30(3-4), 129-132

Basey, Marleeta F(2004). Flour Power: a Guide to Modern Home Grain Milling. Albany, Or.: Jermar.

Becaria, A., Campbell A. and Bondy, S. C (2002). Aluminum as a toxicant. Toxicol Ind Health. 18(7):309–20

Beltcheva, M., Metcheva, R., Popov, N (2012) Modified natural clinoptilolite detoxifies small mammal's organism loaded with lead I. Lead disposition and kinetic model for lead bioaccumulation. Biological Trace Element Research. 147(1-3):180–8

Bernhoft, R. A (2012) Mercury toxicity and treatment: a review of the literature. J Environ Public Health. 460508

Bhaskaram, P (2001) Immunobiology of mild micronutrient deficiencies. British Journal of Nutrition, 85 (2, Supplement), S75-80.

Bjermo H, Sand S, Nälsén C, Lundh T, Enghardt Barbieri H, Pearson M, Lindroos AK, Jönsson BA, Barregård L, Darnerud PO (2013). Lead, mercury, and cadmium in blood and their relation to diet among Swedish adults. Food Chem Toxicol. 57:161-9

Bronstein, A. C., Spyker, D. A., Cantilena, L. R., Jr, Rumack, B. H., and Dart, R. C. (2011) Annual Report of the American Association of Poison Control Centers' National Poison Data System (NPDS): 29th Annual Report. Clin Toxicol (Phila). 50(10):911–1164

Buchko GW, Hess NJ, Kennedy MA (2000) Cadmium mutagenicity and human nucleotide excision repair protein XPA: CD, EXAFS and (1) H/ (15) N-NMR

University of Ghana http://ugspace.ug.edu.gh

spectroscopic studies on the zinc (II) - and cadmium (II)-associated minimal DNA-binding domain (M98-F219). Carcinogenesis. 21(5):1051-7

Caravati, E. M., Erdman, A. R., Christianson, G (2008) Elemental mercury exposure: an evidence-based consensus guideline for out-of-hospital management. Clin Toxicol (Phila). 46(1):1–21

CDC (2012) Response to Advisory Committee on Childhood Lead Poisoning Prevention Recommendations in "Low Level Lead Exposure Harms Children: A Renewed Call of Primary Prevention",. Centers for Disease Control and Prevention. Available online: http://www.cdc.gov/nceh/lead/ acclpp/CDC_Response_Lead_Exposure_Recs.pdf [Accessed on October 23, 2013].

CDC. [Accessed August 15, 2013b]. Center for Disease Control Lead. Cdc.gov. Available at: http://www.cdc.gov/nceh/lead/

CDC. Updated Tables March 2013a Centers for Disease Control. Fourth National Report on Human Exposure to Environmental Chemicals, 1–324.

CDC. (2009) Centers for Disease Control.Fourth National Report on Human Exposure to Environmental Chemicals. 1–529

Chary, N. S., Kamala, C. T. and Raj, D. S. (2008). Assessingrisk of heavy metals from consuming food grown on sewageirrigated soils and food chain transfer. Ecotoxicology andEnvironmental Safety, **69 (3)**, 513–524.

Chen ZS (2000). Relationship between heavy metal on concentrations health risk due to dietary intake of heavy metals in the industrial area of Huludao City, China. Sci. Total Environ. 387, 96–104.

Copat, C., Bella, F., Castaing, M., Fallico, R., Sciacca, S. andFerrante, M. (2012). Heavy Metals Concentrations in Fishfrom Sicily (Mediterranean Sea) and Evaluation of PossibleHealth Risks to Consumers. Bull. Environ. Contam. Toxicol.**88**, 78–83.

CPSC. United States Consumer Product Safety Commission.Total Lead Content. Available at: http://www.cpsc.gov/lead. Accessed 10/29/2013.

Crisponi, G., Dean, A., Di Marco, V. (2013) Different approaches to the study of chelating agents for iron and aluminium overload pathologies. Anal Bioanal Chem. 405(2-3):585–601

Cuadrado, J. Kumpulainen, A. Carbajal, O (2000). Moreiras Cereals contribution to the total dietary intake of heavy metals in Madrid, Spain J. Food Comp. Anal., 13, pp. 495–503

IAEA (2001). Cytogenetic Analysis for radiation Dose Assessment, Technical Report Series No.405,

University of Ghana http://ugspace.ug.edu.gh

Davenward S, Bentham P, Wright J, Crome P, Job D, Polwart A, Exley C (2013). Silicon-rich mineral water as a non-invasive test of the 'aluminum hypothesis' in Alzheimer's disease. *Journal of Alzheimer's disease: JAD.* 33(2):423-430.

Dean, John A and Rains, Theodore C (1969) Flame Emission and Atomic Absorption Spectroscopy, Vol. 1–Theory and Vol. 2–Components and Techniques, Marcel Dekker.

Defilippis, A. P., Blaha, M. J., and Jacobson, T. A (2010) Omega-3 Fatty acids for cardiovascular disease prevention. Curr Treat Options Cardiovasc Med. 12(4):365–80

DOH. Department of Health. Lead in Children's Toys: Questions and Answers for Parents.Availableat:http://www.health.ny.gov/environmental/lead/recalls/questions_and_answers.htm. Last updated 8/2007. Accessed 10/29/2013.

Dongiovanni P, Fracanzani AL, Fargion S, Valenti L (2011 Oct). Iron in fatty liver and in the metabolic syndrome: a promising therapeutic target.J Hepatol. 55(4):920-32

Duffus, J. H (2002) "Heavy Metals"—A Meaningless Term? Pure Appl. Chem. 74(5):793–807

Ellervik C, Tybjaerg-Hansen A, Nordestgaard BG (2012 Jan) Risk of cancer by transferrin saturation levels and haemochromatosis genotype: population-based study and meta-analysis. J Intern Med. 271(1):51-63

EPA. United States Environmental Protection Agency. Lead in Toys and Jewelry. Available at: http://www2.epa.gov/lead/lead-toys-and-toy-jewelry. Last updated 2/14/2013. Accessed 10/29/2013.

Ercal, N., Gurer-Orhan, H., and Aykin-Burns, N (2001) Toxic metals and oxidative stress part I: mechanisms involved in metal-induced oxidative damage. Curr Top Med Chem. 1(6):529–39

European Union, (2006). Setting maximum levels for certain contaminants in foodstuffs, Commission Regulation (EC) No 1881/2006; OJ L 364, 20.12.2006, p. 5
European Union, 2006.Commission Regulation (EC) No. 1881/2006 of 19 December 2006 Setting Maximum Levels for Certain Contaminants in foodstuffs. Off. J. Eur. Union L. 364, 5–24.

FDA.U.S. Food and Drug Administration.About Dental Amalgam Fillings.FDA webpage.Availableat:http://www.fda.gov/medicaldevices/productsandmedicalprocedures/dentalproducts/dentalamalgam/ucm171094.htm. Last updated 8/11/2009. Accessed 10/29/2013.

University of Ghana http://ugspace.ug.edu.gh

Flowers JL, Lonsky SA, Deitsch EJ (2009) Clinical evidence supporting the use of an activated clinoptilolite suspension as an agent to increase urinary excretion of toxic heavy metals.*Nutrition and Dietary Supplements.* 11-18.

Food and Agriculture Organization [FAO]. 2001. Codex Alimentarius Commission Food Additives and Contaminants. FAO/WHO, Rome, Italy. ALINORM 01/12A: 1-289.

Food and Agriculture Organization of the United Nations.*The State of Food Insecurity in the World 2005*. . Retrieved from http://www.fao.org/docrep/008/a0200e/a0200e00.htm on 2006-09-29.

Frazzoli CD, Marilena, Amato, S Caroli (2007). Arsenic and other potentially toxic trace elements in rice. The determination of chemical elements in food: Applications for atomic and mass spectrometery Jhon W iley and sons, Inc. 12:383-397

Galanis, A., Karapetsas, A., and Sandaltzopoulos, R. (2009) Metal-induced carcinogenesis, oxidative stress and hypoxia signalling. Mutat Res. 674(1-2):31–5

Gallagher, C. M. C., and Meliker, J. R. J (2012) Mercury and thyroid autoantibodies in U.S. women, NHANES 2007-2008. Environ Int. 40:39–43

Gillette Guyonnet, S., Andrieu, S., and Vellas, B. (2007) The potential influence of silica present in drinking water on Alzheimer's disease and associated disorders. J Nutr Health Aging. 11(2):119–24

Haas, J. & Brownlie, T. (2001) Iron deficiency and reduced work capacity: a critical review of the research to determine a causal relationship. J. Nutr. 131:676S-690S.

Handler, P. P., and Brabander, D. D. (2012) Increased Incidence and Altered Risk Demographics of Childhood Lead Poisoning: Predicting the Impacts of the CDC's 5 µg/dL Reference Value in Massachusetts (USA). Int J Environ Res Public Health. 9(11):3934–42

Hewitt CD, Savory J, Wills MR. (1990) Aspects of aluminum toxicity. Clin Lab Med. Jun; 10(2):403-22

Houston, M. C (2011) Role of mercury toxicity in hypertension, cardiovascular disease, and stroke. J Clin Hypertens (Greenwich). 13(8):621–7

Ibrahim, D., Froberg, B., Wolf, A., and Rusyniak, D. E (2006a). Heavy Metal Poisoning: Clinical Presentations and Pathophysiology. Clinics in Laboratory Medicine. 26(1):67–97

Jang, D. H., and Hoffman, R. S (2011). Heavy metal chelation in neurotoxic exposures. Neurol Clin. 29(3):607–22

Jenkins, Ron, X-Ray Fluorescence Spectrometry. 1988, John Wiley & Sons, Inc. QD96.X2J47 ISBN 0-471-83675-3.

University of Ghana http://ugspace.ug.edu.gh

Johnson W., (1977), Metallurgy, 5th Edition, U.S.A., Technical Publishers Inc,pp269, 278-279.

Jones, Hannah. "Cereal Grain Quality." (2010) Our Daily Bread: Following Grains Through The Food System. Organic Research Centre, Hamstead Marshall, England. 12 Aug. 2010.

Jurkic, L. M., Cepanec, I., Paveli? S. K., and Paveli?, K. (2013) Biological and therapeutic effects of ortho-silicic acid and some ortho-silicic acid-releasing compounds: New perspectives for therapy. Nutr Metab. 10(1):2

Kallianpur AR, Hall LD, Yadav M, Christman BW, Dittus RS, Haines JL, Parl FF, Summar ML. (2004) Increased prevalence of the HFE C282Y hemochromatosis allele in women with breast cancer. Cancer Epidemiol Biomarkers Prev. 13(2):205-12

Kikuchi Y, Nomiyama T, Kumagai N, Uemura T, Omae K (2002) Cadmium concentration in current Japanese foods and beverages. J. Occup. Health. 44:240-247.

Kirberger, M., Wong, H. C., Jiang, J., and Yang, J. J. (2013) Metal toxicity and opportunistic binding of Pb(2+) in proteins. J. Inorg. Biochem. 125:40–9

Koedrith, P. and Seo, Y. R (2011) Advances in carcinogenic metal toxicity and potential molecular markers. Int J Mol Sci. 12(12):9576–95

Koller K, Brown T, Spurgeon A, Levy L. (2004) Recent developments in low-level lead exposure and intellectual impairment in children. Environ Health Perspect. 112(9):987-94

Kontoghiorghes GJ, Pattichis K, Neocleous K, Kolnagou A. (2004) The design and development of deferiprone (L1) and other iron chelators for clinical use: targeting methods and application prospects. *Current medicinal chemistry.*Aug 11(16):2161-2183.

Kremastinos, D. T., and Farmakis, D. (2011) Iron overload cardiomyopathy in clinical practice. Circulation. 124(20):2253–63

Kwofie, S. and Chandler, H. D. (2006) "A po-tential health effects of locally manufac-tured corn-mill grinding plates", *J. Sci-ence and Tech. 26 (2): 137-147.*

Lanre –Iyanda IYand Adekunle IM, (2012) Assessments of heavy metals and their estimated dietary intakes from two commonly consumed foods (kulikuli and Robo) Found in Nigeria: Africa Journal of food, Agriculture, Nutrition and Development.

Lemire, J., and Appanna, V. D (2011) Aluminum toxicity and astrocyte dysfunction: a metabolic link to neurological disorders. J. Inorg. Biochem. 105(11):1513–7

Li, Y.-F., Dong, Z., Chen, C. (2012) Organic selenium supplementation increases mercury excretion and decreases oxidative damage in long-term mercury-exposed residents from Wanshan, China. Environ Sci Technol. 46(20):11313–8

University of Ghana http://ugspace.ug.edu.gh

Lin, C. S., Boltz, R. C., Siekierka, J. J., & Sigal, N. H. (1991) Cell. Immunol.133, 269-284.

Lipton ES and Barboza D. As More Toys Are Recalled, Trial Ends in China. The New York Times online. World Business web page. Available at: http://www.nytimes.com/2007/06/19/business/worldbusiness/19toys.html?pagewanted=all&_r=1&. 6/19/2007. Accessed 10/29/2013.

Lokko P., Kirkmeyer S. and Mattes R.D., (2004), A cross-cultural comparison of appetitive and dietary responses to food challenges, Food Quality and Preference, Vol. 15, Issue 27: pp.129–I36.

Machiwa JF(2010). Heavy metal levels in paddy soils and rice (Oryza sativa) from wetlands of lake victoria basin, tanzania. Tanz. J. Sci. (36):451-459

Manton, W. I., Angle, C. R., Stanek, K. L., Reese, Y. R., and Kuehnemann, T. J. (2000) Acquisition and retention of lead by young children. Environ. Res. 82(1):60–80

Martinez-Zamudio R, Ha HC. (2011) Environmental epigenetics in metal exposure.*Epigenetics: official journal of the DNA Methylation Society.* 6(7):820-827.

May, J. B., (1986) "Wet Milling: Process and Products,"Corn Chemistry and Technology, S.A.Watson and P.E.Ramstad (eds.) (St. Paul, MN: Amer-ican Association of Cereal Chemists.

Miranda ML, (2011) Anthopolos R, Hastings D. Environ Health Perspect. A geospatial analysis of the effects of aviation gasoline on childhood blood lead levels. 119(10):1513-6

Miranda, M. L. (2010) Edwards, S. E., Swamy, G. K., Paul, C. J., and Neelon, B. Blood Lead Levels Among Pregnant Women: Historical Versus Contemporaneous Exposures. Int J Environ Res Public Health. 7(4):1508–19.

Mmolawa, K.B., Likuku, A. S. and Gaboutloeloe, G. K. (2011) Assessment of Heavy metal pollution in soil along major roadside areas in Botswana. African Journal of Environmental Science and Technology, 5(3):186-196.

Montinaro, M., Uberti, D., Maccarinelli, G., Bonini, S. A., Ferrari-Toninelli, G., and Memo, M. (2013) Dietary zeolite supplementation reduces oxidative damage and plaque generation in the brain of an Alzheimer's disease mouse model. Life Sci. 92(17-19):903–10

National Research Council, (1989), Recommended dietary Allowance, 9th Edition, Food and Nutrition Board, NRC, National academy Press, Washington DC, pp547

Nelson RL, Davis FG, Persky V, Becker E. (1995) Risk of neoplastic and other diseases among people with heterozygosity for hereditary hemochromatosis.Cancer. 1;76(5):875-9

University of Ghana http://ugspace.ug.edu.gh

Nierenberg DW, Nordgren RE, Chang MB, et al. (1998) Delayed cerebellar disease and death after accidental exposure to dimethylmercury. New England Journal of Medicine. 338(23):1672–1676

Nogué S, Sanz-Gallén P, Torras A, Boluda F (2004) Chronic overexposure to cadmium fumes associated with IgA mesangial glomerulonephritis. Occup Med (Lond). 54(4):265-7

Park JD, Zheng W. (2012) Human exposure and health effects of inorganic and elemental mercury. J Prev Med Public Health. 45(6):344-52

Percy, M. E., Kruck, T. P. A., Pogue, A. I., and Lukiw, W. J. (2011) Towards the prevention of potential aluminum toxic effects and an effective treatment for Alzheimer's disease. J. Inorg. Biochem. 105(11):1505–12

Pitts, A.G., Van Loon, J.C. and Beamish, F.E., (1970) Anal. Chim. Acta., 50, 181; 50, 195.

Reddy CC, Scholz RW, Massaro EJ. (1981) Cadmium, methylmercury, mercury, and lead inhibition of calf liver glutathione S-transferase exhibiting selenium-independent glutathione peroxidase activity.*Toxicology and Applied Pharmacology*. 61(3):460-468.

Rodrigues EG, Virji MA, McClean MD, Weinberg J, Woskie S, Pepper LD. (2010) Personal exposure, behavior, and work site conditions as determinants of blood lead among bridge painters. J Occup Environ Hyg. 7(2):80-7

Rossiter S. Keeping Kids Safe from Toys Contaminated with Lead. Available at: http://www.colorado.gov/cs/Satellite?blobcol=urldata&blobheadername1=Content-Disposition&blobheadername2=Content-Type&blobheadervalue1=inline%3B+filename 3D%22Keeping+Kids+Safe+from+Toys+Contaminated+with+Lead.pdf% 22&blobheadervalue2=application%2Fpdf&blobkey=id&blobtable=MungoBlobs&blobwhere=1251811829567&ssbinary=true. Accessed 10/29/2013.

Rusyniak DE, Furbee RB, Kirk MA (2002) Thallium and arsenic poisoning in a small midwestern town. Ann Emerg Med. 39(3):307-11

Rusyniak, D. E., Arroyo, A., Acciani, J., Froberg, B., Kao, L., and Furbee, B. (2010) Heavy metal poisoning: management of intoxication and antidotes. EXS. 100:365–96

Sahinbegovic E, Dallos T, Aigner E, Axmann R, Manger B, Englbrecht M, Schöniger-Hekele M, Karonitsch T, Stamm T, Farkas M, Karger T, Stölzel U, Keysser G, Datz C, Schett G, Zwerina J. (2010) Musculoskeletal disease burden of hereditary hemochromatosis. Arthritis Rheum. 62(12):3792-8

Sällsten G, Kreku S, Unosson H. (2000) A small dose of ethanol increases the exhalation of mercury in low-level-exposed humans. J Toxicol Environ Health A. 26;60(2):89-100

University of Ghana http://ugspace.ug.edu.gh

Seppanen K, Kantola M, Laatikainen R, Nyyssonen K, Valkonen VP, Kaarlopp V, Salonen JT. (2000) Effect of supplementation with organic selenium on mercury status as measured by mercury in pubic hair. Journal of trace elements in medicine and biology : organ of the Society for Minerals and Trace Elements (GMS). 14(2):84-87.

Shar, G. Q., Kazi, T. G., Jakhrani, M. A., Sahito, S. R., & Memon, M. A. (2002). Determination of seven heavy metals, cadmium, cobalt, chromium, nickel, lead, copper and manganese in wheat flour samples by flame atomic absorption spectrometry. Journal of the Chemical Society of Pakistan, 24(4), 265–268.

Shelleh, H. H. (2012) Depleted Uranium. Is it potentially involved in the recent upsurge of malignancies in populations exposed to war dust? Saudi Med J. 33(5):483–8

Siddique A, Kowdley KV. (2012) Review article: the iron overload syndromes. Aliment Pharmacol Ther. 35(8):876-93

Sigel, A., Sigel, H., and Sigel, R. (2013) Cadmium: from toxicity to essentiality.

Sinicropi, M. S., Amantea, D., Caruso, A., and Saturnino, C (2010) Chemical and biological properties of toxic metals and use of chelating agents for the pharmacological treatment of metal poisoning. Arch Toxicol. 84(7):501–20

Skoog, Douglas A.; Holler, F. James; Nieman, Timothy A. (1998) Principles of Instrumental Analysis. Fifth Edition, Thomson Learning, Inc. ISBN 0-03-002078-6.

Thévenod, F. and Lee, W.-K. (2013) Toxicology of cadmium and its damage to mammalian organs. Met Ions Life Sci. 11:415–90

Topashka-Ancheva, M., Beltcheva, M., Metcheva, R., (2012) Modified natural clinoptilolite detoxifies small mammal's organism loaded with lead II: genetic, cell, and physiological effects. Biological Trace Element Research. 147(1-3):206–16

USEPA, (2009).United States Environmental Protection Agency, Risk-based concentration table. Philadelphia: United States Environmental Protection Agency,Washington, DC.

VARIAN. Publication No 85- 100009-00 Revised March 1989.

Wang X, Sato T, Xing B, Tao S (2005) Health risks of heavy metals to the general public in Tianjin, China via consumption of vegetables and fish. Sci Total Environ 350: 28–37

Welz, B., 1985 Atomic Absorption Spectrometry, 2nd Edition, VCH Verlagsgesellschaft, Weinheim.

Whanger PD. (1992) Selenium in the treatment of heavy metal poisoning and chemical carcinogenesis.Journal of trace elements and electrolytes in health and disease. 6(4):209-221.

University of Ghana http://ugspace.ug.edu.gh

FAO/WHO (2006) Evaluation of certain food contaminants. Sixty-fourth report of the Joint FAO/WHO Expert Committee on Food Additives (JECFA) Geneva, World Health Organization, International Programme on Chemical Safety (WHO Technical Report Series, No. 930; http://whqlibdoc.who.int/trs/WHO_TRS_930_eng.pdf, accessed 19 August 2010)

Worley, J. and Kveeh, S, (2011) Inductively couple plasma mass spectroscopy. Retrieved from htt://www.cee.vt.edu/ewr/environmental/teach/smprimer/icpms/icpms.htm.

Wright, R. O., and Baccarelli, A. (2007) Metals and neurotoxicology.Journal of Nutrition. 137(12):2809–13

Wu Z, Du Y, Xue H, Wu Y, Zhou B. (2012) Aluminum induces neurodegeneration and its toxicity arises from increased iron accumulation and reactive oxygen species (ROS) production. Neurobiol Aging. 33(1):199.e1-12

Wyasu G. and O. A. Kure,(2012).Determination of organic pollutants in hospital wastewater and food samples within Ahmadu Bello University Teaching Hospital (Abuth), Shika, Zaria-Nigeria Advances in Applied Science Research, 3 (3):1691-1701

Xue, Z.J.; Liu, S.Q.; Liu, Y.L.; Yan, Y.L. 2012.Health risk assessment of heavy metals for edible parts of vegetables grown in sewage-irrigated soils in suburbs of Baoding City, China.Environmental Monitoring and Assessment 184: 3503- 3513.

Zheng, N., Wang, Q., Zhang, X., Zheng, D., Zhang, Z., Znang, S., 2007. Population

Zukowska J, Biziuk M (2008) Methodological Evaluation of Method for Dietary Heavy Metal Intake. *J Food Sci* **73**(2)**:**R21-R29.

Zwolak, I., and Zaporowska, H. (2012) Selenium interactions and toxicity: a review. Selenium interactions and toxicity. Cell Biol. Toxicol. 28(1):31–46