AN ANALYSIS WITH X-RAY FLUORESCENCE (XRF) SPECTROMETRY TO DETERMINE ELEMENTAL TOXINS IN MANUFACTURED PRODUCTS

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TABLE OF CONTENTS

LIST OF TABLES

Table Page

LIST OF FIGURES

CHAPTER I

BACKGROUND

This investigation will involved the analysis of multiple samples of manufactured products, utilizing x-ray fluorescence spectrometry (XRF) to determine if elemental toxins are present. The elemental toxins specifically focused on will be lead, bromine, and mercury. This analysis will be very important to the consuming public at large, the medical community, and the U.S. Environmental Protection Agency, (2007) because the manufactured products sampled will specifically be those that are either edible or intended for close oral contact, and that target children six and younger. This is the sub group within the population at most risk, according to Ellenhorn (1997). Two groups of materials will be compared, consisting of manufactured products made in the United States and those imported from countries other than the United States.

Anecdotal reports have surfaced continually over the last decade as reported by The New York City Department of Health and Mental Hygiene, (2008)[a] which has conducted laboratory analysis of manufactured products from China that have shown high levels of mercury or lead. In addition, mercury has been released over recent years into the atmosphere at an alarming rate by China, (Pottinger et al., 2004) where deposition into water systems could impact human health.

More stringent controls should be placed on imported and domestic manufactured products especially those intended for use by small children and infants, Salazar (2007). This is, Salazar stated, opposed to just recalling an item after poisoning has occurred. Infants and small children will suffer long term mental and physical damage from exposure to elemental toxins as they are the most vulnerable group within the population (Ellenhorn, 1997) where the detrimental effects to this sub group are described.

Imports into the United States were growing at an exponential rate explained (Sheth, 2007) while rigorous safety controls on this ponderous issue have not kept pace. In addition, the United States is plagued with many Super Fund sites as discussed by, The Center for Hazardous Substance Research (2008) where elemental toxins have been documented leaching into surrounding water systems. Water is recognized as a universal solvent flowing literally everywhere on the planet and is also a major component of food items, (Industrial Water Use, 2005) including fabricating, processing, and washing, diluting and cooling.

In response to this environmental problem, the U.S. Environmental Protection Agency (2007) has implemented new policies in the wake of increased elemental toxins in the environment as they recognize the group at most risk from this contamination is small children and infants. The Food Quality Protection Act (FQPA) requires the U.S. Environmental Protection Agency (2007), to consider risks to infants and children when setting tolerance levels for toxins in the environment. In accordance with FQPA, all tolerance decisions will take into account children's special susceptibility to pesticides some of which might contain bromine. The EPA has outlawed the use of several pesticides on many "kid" foods, such as apples, when grown in the United States and utilizes an

additional tenfold (10X) safety factor as appropriate in setting tolerances. The U.S. Environmental Protection Agency (2007) stated in their report, in reference to children and infants, that there are "critical periods" in human development when exposure to a toxin can permanently alter the way an individual's biological system operates.

As the globalization of trade has grown exponentially in recent decades, Warner (2005) reported specifically on the growing percent of apples and apple products such as concentrated apple juice (CAJ) imported into the United States from China. She stated that in 1995, China held only five percent of the market share of CAJ in the world. It now claims 53% of the market in the world's apple market. Political pressures world-wide serve different agendas than that of children's health when deciding the future use of elemental toxins, like the bromide contained in pesticides. Hileman (2004) described what had occurred at a United Nations meeting in Montreal, explaining that 114 countries agreed to grant permission to 11 developed countries to continue employing the pesticide Methyl Bromide for so-called critical uses even though this toxin was certified as a known carcinogen in the United States and could potentially find its way into manufactured products. Poelarends et al. (1999) explained that even well-documented toxins are still produced in large amounts for use as a lead scavenger in some countries and as a fumigant for stored grain. One extreme case of poisoning occurred in Iraq when grain fumigated with a compound containing mercury was mistakenly used to make bread, as reported by the Center for the Evaluation of Risks to Human Reproduction (2008). This agency reported that in the fall and winter of 1971-72, wheat seed intended for planting that had been treated with an alkyl mercury fungicide was mistakenly used to prepare bread; and more than 6,500 Iraqis were hospitalized with neurological symptoms and 459 died from

this toxic poison mistakenly being used in a manufactured food item. Edible manufactured products, typically sold to wholesalers or retailers for distribution to consumers, have been designed so that the entire item is taken internally, where its individual elemental make-up will thus be absorbed into the body. Other products not specifically designed to be consumed, however are yet intended to have close oral contact. Both types of manufactured products (Industrial Water Use, 2005), use large amounts of water in manufacturing process.

The three elemental toxins this research focuses on all have well-documented research indicating their extreme toxicity to children and infants. Lead in or on a manufactured product could pose a poisoning threat as explained by Perez (2008). Perez stated that children get lead in their bodies when they put lead objects in their mouths, or they can get lead poison on their fingers from touching a dusty or peeling lead object, and then putting their fingers in their mouths. Perez also stated that tiny amounts of lead can be inhaled.

Bromine is incorporated into a variety of salts as a bactericide (Korslin, 2003) in potable water and in organic compounds where it is utilized as a potent pesticide, CDC Home (1992) in agricultural venues. Poelarends et al. (1999) discussed that bromine compounds have been detected in ground water and described them as “extremely toxic xenobiotic”.

China has undergone a dramatic shift toward industrialization within the last few decades (Pottinger, 2004) and, with the resultant pollution, is also becoming a global poisoning concern. Mercury is being released from China’s accelerated power industry,

mostly fueled by coal, leading to the buildup of mercury in the world's water and food supply.

It will be hypothesized that some samples of manufactured products when analyzed will show higher levels of lead, bromine or mercury than currently are allowed by FQPA/EPA standards for consumption in the United States.

The Problem

To what extent will imported manufactured products and best fit manufactured products made in the United States, intended for oral consumption or close oral contact which target children six and under, when analyzed will have significant levels of elemental toxins specifically lead, bromine and mercury?

Rationale for the Study

The rationale for this study will be to determine the facts regarding elemental toxins in samples of manufactured products. BenKinney (2008) discussed the present dangers of known and newly identified chemicals in food stuffs and the need to develop methods for detecting these chemical contaminates. BenKinney (2008) reported that, on the entire planet with multiple countries' governments leading the way, there is a refocusing on the threat of toxicological implications, that people might have when they are exposed to known and new unknown toxins. There have been defined as synthetic or even naturally occurring chemicals that might cause adverse effects to humans or to the environment.

In addition, BenKinney (2008) shared a report from the CDC (Center for Disease Control) that outlines a dramatic increase in chemical contaminates from 2001 to the

present. These chemicals, BenKinney stated, could have public health implications. The CDC described recent increases of chemical contaminates, stating that they have "risen exponentially". BenKinney (2008) extrapolated and listed each sequential year's totals of chemical contaminates since the first published reports that were issued in 2001. This aforementioned report stated that in 2001 only 27 chemicals were deemed in need of biomonitoring. However in 2003 this number had risen to 116, and in 2005, 148 chemicals were raising concerns. The newest report, BenKinney (2008) stated, is due out in 2008 with a staggering 275 different chemical contaminates of high concern to human health. The CDC report on human's possible exposure to chemicals as reported by BenKinney (2008) called this steep growth curve exponential.

Samples of manufactured products analyzed in this study will be limited to those that specifically target small children and infants. According to Salazar (2007) currently, when a dangerous product is found to contain a chemical contaminate, the only action taken is to block its import and force a recall if it has already been sold. But stopping the problem at its source before it causes injuries is much more difficult, Salazar states, and even more so because China is the biggest offender. However it is not the only one. The United States has turned away tainted products from Mexico, India, and from elsewhere around the world. Salazar (2007) elucidates that a much greater effort must be made to identify tainted products before they ever reach the consumer.

In the United States, a complex system of many overlapping agencies has been given the charge of protecting the entire food supply. This consists of the following list of agencies each with a specific focus as reported by Rawson & Vogt (1998) who explained that multiple government agencies are responsible for ensuring the safety of the United

States food supply. This includes both imported and domestic production of food items. The main agency is the Food and Drug Administration (FDA) which is a division of the Department of Human Services (DHHS). Another branch of these agencies is the Food Safety and Inspection Service (FSIS) which falls under the umbrella of the United States Department of Agriculture (USDA). Together the FDA and the USDA combine to function as a safety net responsible for approximately 90% of the watch dog services of the United States food supply. The remaining smaller percents are facilitated by less known but vital agencies, for example the National Marine Fisheries Service which is a sub branch under the United States Department of Commerce (DOC) which controls and inspects fresh fish.

Rawson and Vogt (1998) also included in this report an explanation that the FDA's total inspection force is roughly only 800 people and they are located in field offices spread over 49 states, the District of Columbia, and Puerto Rico.

Haaland (2007/2008) explained the complex history of these interwoven agencies and their formations, explaining that the FDA was originally founded by President Roosevelt in 1906 after the conditions in the Chicago stock yards were published in Upton Sinclair's book "The Jungle." Subsequently the Environmental Protection Agency was also created in response to the written accounts of pesticides and their detrimental effects in Rachel Carson's, *Silent Spring*. Haaland (2007/2008) interprets the multiple agencies and their over lapping web of protections explaining that once a government agency is created it never is replaced or absorbed it is just added to the grouping of agencies that function within the United States government.

Within the same publication, Haaland (2007/2008) discussed increases in foreign suppliers and globalization of the food supply. Haaland (2007/2008) stated that recalls of food tainted by wheat gluten from China containing melamine highlighted the worldwide interconnectedness of today's food system. Haaland elucidated with this example that new risks to the food supply are a current and omnipresent concern.

Objectives of the Study

1. One objective of this study is to measure scientifically and accurately the amount, if any, of the elemental toxins lead, bromine, and mercury contained in samples of manufactured products. These products are limited to those intended for oral consumption or close oral contact by a small child under the age of six, or an infant.

2. In addition, another objective is to compare elemental toxins found in manufactured products imported into the United States with those toxins found in manufactured products labeled as made in the United States.

3. An objective is to verify the presence of three known and well-researched elemental toxins: lead, bromine, and mercury. These elemental toxins levels, if any, are compared to the United States government-published allowable limits of each.

4. In addition, other elemental toxins, if any, are notated and indicated by the X-Ray fluorescent spectrograph (XRF).

5. A final objective is to make the readers of this study aware of the findings of this analysis and, in so doing, to facilitate awareness of the current levels of elemental toxins found in samples of manufactured products that specifically target small children and infants when purchased in the United States. If significant elemental toxins are found

to be present, suggestions will be made to better ensure the safety of this sub group's potential food supply.

Significance of the Study

Young children and infants are susceptible to elemental toxins because their brains and bodies are not fully developed. Silverman and Fodera (2007) explained that the greatest risk of injury from lead poisoning is to children under the age of seven, whose developing bodies and brains are sensitive to even small amounts of lead. Bone and organ development can also be negatively and, in some cases, irreversibly affected when the body deposits heavy metals (Appleton, 2000). After a lifetime of exposure, lead is stored in the bones where it is mistaken for calcium in multiple sites.

Some common elements might be necessary in trace amounts, but would overload anatomical systems if ingested in large amounts. Others serve no function of any kind in a healthy body. Living on Earth (2007) explained, for example, that there is no required concentration of lead within any anatomical system. "Lead is what scientists call xenophobic – a foreign substance with no useful role in human physiology, toxic even in minute quantities" (Curwood, 2003).

Mounting evidence shows that tainted products are making their way into the United States, explained Woolf and Woolf, (2005) who further discussed families where children were poisoned by lead-contaminated spices. Pottinger et al. (2004) also warned that among the biggest worries world-wide is the impact of China's vast and growing power industry that, through the burning of dirty coal, contributes to the buildup of mercury in the world's water and food supply. Young children and infants, Ellenhorn

(1997) states, are affected by even moderate increases in body lead which adversely affect IQ. Ellenhorn (2007) a dominate authority on toxicology world wide specifically reported on pesticide residue as it relates to infants or small children. Ellenhorn (2007) explained that the USDA sets a higher standard for this sub group of the population. This government agency sets a ten fold increase in additional safety factors for possible contaminated within food items that target this most vulnerable group. This reference text for physician's further spelled out that infants and small children have special sensitivity to chemical contaminates, as the dose makes the poison.

Conceptual Assumptions

The following assumptions will be made

1. No alterations such as tampering, once they were sealed in their country of origin have been made to the manufactured items at any point

2. The X-ray Fluorescence Spectrometer (XRF) in use in the Physical Science building at Oklahoma State University is a true and correct detection device to measure amounts of elemental toxins such as lead, bromine, mercury and others in a sample into the parts per billion and the hand held Niton® XRF is also a reliable instrument for analysis.

3. No errors or contaminations will accidentally be made in sampling technique as each sample subsequently loaded in the (XRF).

4. An honest effort will be made to randomly sample items found in various stores over the time prescribed.

5. The sample containers, catalog number: 3529, 31mm X-cells from CertiPrep are not contaminated and will only be used once for each individual sample.

6. New disposable individual gloves will be used for the handling of each sample to avoid any contamination.

7. The researcher will be well trained and assisted by her supervising professor of chemistry, Dr. Allan Apblett, and be able to verify this researcher's data presented by the X-ray Fluorescence Spectrometer accurately under his expert guidance.

8. Samples will be carefully stored and sealed in zip lock bags to preserve their composition, and identical items used for a control will be also carefully kept sealed in order that they may at some future time be used to verify elemental toxins if requested.

Definition of Terms

1. Acetic Acid— (Morris, W. (Ed.). (1970) A clear colorless organic acid with a distinctive pungent odor.

2. Acrodynia—(Morris, W. (Ed.). (1970). Term used in medicine that is translated as painful extremities referring to pain in the hands and feet of the victim of mercury poisoning. From the Greek akros, topmost extreme; acro: an extremity of the body.

3. "Best Fit"— (Results for fit, 2007). Adjective Consistent with prevailing or accepted standards or circumstances; appropriate.

4. Bivalent—(Morris, W. (Ed.). (1970). *adj.* Chemistry. Having valence two.

5. Blood Lead Level (BLL) (Understanding your Childs lead test. (n.d.). Blood test determining amount of lead in the blood at the time of testing. It is used to screen for

exposure to harmful levels of lead. It may also be ordered to monitor the effectiveness of treatment and to confirm that lead levels are decreasing over time.

6. Bromine — (Daintith, 1996).-A halogen element. At room temperature, it is a red volatile liquid.

7. Bromism—(Morris, W. (Ed.). (1970). Also brominism. Poisoning from overuse of bromines. Symptoms include: skin eruptions, headache, sleeplessness, apathy, and loss of strength.

8. Entropy—(Morris, W. (Ed.). (1970)-The measure of the capacity of a system to undergo spontaneous change.

9. Fudge Factor—(Definition of fudge: verb.2000). English slang meaning to go beyond the proper limits of something.

10. Inert—(Morris, W. (Ed.). (1970) -3. *Chemistry.* a. Exhibiting no chemical activity; totally nonreactive.

11. Lead — (Daintith, 1996).-Symbol Pb. A heavy dull grey soft ductile metallic element belonging to group 14 of the periodic table.

12. Malleable——(Morris, W. (Ed.). (1970)-1. Capable of being shaped or formed, as by hammering or pressure: *a malleable metal.*

13. Matrix Effect- (XRF Web Seminar [Module 2: Basic XRF Concepts]. (n.d.) – Physical matrix effects result from variations in the physical character of the sample. These variations may include such parameters as particle size, uniformity, and surface condition. One way to reduce error associated with variation in particle size is to grind all samples to a uniform particle size. Chemical matrix effects result from the difference in the concentrations of interfering elements.

14. Methyl mercury— (Nadakavukaren, 2006). A highly toxic, readily soluble form of mercury resulting from inorganic metallic mercury being introduced into an aerobic aquatic system. Metallic mercury is taken in and converted into Methyl Mercury by the bacterium *Methanobacterium amelanskis,* and thus begins moving through the aquatic food chain, becoming more concentrated at each higher trophic level.

15. Mercury— (Daintith, 1996).-Symbol Hg. A heavy, silvery, liquid metallic element belonging to the zinc family.

16. Minamata disease—(Nadakavukaren, 2006). Terminology given to mercury poisoning that occurred after the Chisso Company, a plastic factory in Minamata Japan, released inorganic mercury wastes into Minamata Bay.

17. Parts per billion (ppb) (Expression of analytical results: Chapter 40, 2008). — One part per billion is equal to one-thousandth of one part per million (0.001 ppm).

18. Parts per million (ppm) — (Expression of analytical results: Chapter 40, 2008). One part per million equals one ten-thousandth of one percent (0.0001%), or one part (by weight) in a million parts

19. Plumbism—(Morris, W. (Ed.). (1970)-Chronic lead poisoning

20. (ROI) Region of Interest- Method 6200 Field Portable X-Ray Fluorescence Spectrometry [Environmental Protection Agency online document]. (2007) Each pure, single-element standard is intended to produce strong x-ray peaks. A set of pure element standards for commonly sought analytes is supplied by the manufacturer of an XRF. These standards are used to set the region of interest (ROI) for each element.

21. Tare—(Morris, W. (Ed.). (1970)-The weight of a container or wrapper that is deducted from the gross weight to obtain net weight.

22. Valence electrons- (Morris, W. (Ed.). (1970)-An electron in an outer or next outer shell of an atom that can participate in forming chemical bonds with other atoms.

23. X-ray—(Morris, W. (Ed.). (1970)-A relatively high energy photon with wave length in the approximate range of 0.05 angstroms to 100 angstroms.

24. X-ray Fluorescence Spectrometer—(Daintith, 1996).- A device that focuses X-rays on a given sample, causing the electrons in the lower levels of a sample's electron cloud to absorb this energy and be ejected from the atom. This is followed by a cascade effect of the remaining electrons falling into each empty sub-orbital and, in turn, giving off measurable energy detected by the (XRF). Each element exhibits a unique signature and in this way can be analyzed.

Delimitations

1. This study focuses on items offered for public sale only, in large well-known stores available to the consuming United States public. These include, but are not limited to: Wal-Mart®, Kmart®, Dillon's®, Walgreen's® and Dollar General Stores® and Target®.

2. This research covers items purchased in four states in the United States—Kansas, Oklahoma, and California and Kentucky—as a matter of convenience due to the location of this researcher during the time period for purchasing the items in preparation for research.

3. The research is conducted using the X-ray Fluorescence Spectrometer (XRF) located on the third floor of the Physical Sciences building on the campus of Oklahoma State University in Stillwater, Oklahoma. If a sample is found to have high levels of an elemental toxin as determined by United States government standards, it will be

reanalyzed using a Niton® hand held XRF as provided by the Niton ® Corporation. These two (XRF) analyses will be compared in these cases.

4. The research is limited to 204 total randomly purchased samples of manufactured items. These items will be purchased in pairs, therefore only 102 items will be unique from each other and the other 102 will serve as the controls in this research. Each purchase consists, of two identical manufactured products that meet established criteria found over the time period of twenty months from June 1st 2007 to January 30th 2009. Fifty one items in pairs or 102 total items that have been labeled as manufactured in countries other than the United States were purchased. Additionally, fifty one more items were purchased that consist again of two identical manufactured products that best match items already purchased. The best fit match items will be those that have been labeled as made in the United States. For example, animal crackers manufactured in Mexico, when found, are to be purchased in a quantity of two identical packages. The researcher will then make a diligent search for animal crackers made in the United States, and, again, purchase an identical pair. This will result in the purchase of four sealed packaged manufactured items specifically intended for consumption or use with close oral contact by small children, for each comparison in this research.

5. Items will only be purchased if two identical items are available, as one item will serve as the control in each unit to be tested. Therefore, a total of 204 items will be purchased for this study. This limit is set due to cost and convenience of transportation of the amount of items to be analyzed for elemental toxins.

6. Receipts are to be kept for all items whose samples will remain sealed in their original packages until the time of the random selection of the product that will be testing by coin flip.

7. All items must be non perishable in nature and packaged for long shelf life and be considered a normal item that any prudent adult might have purchased for consumption or use with close oral contact by children six years old and under. These might include soft crackers or baby formula, candies or cartoon shaped pasta and while the diversity of the individual samples will be of great variety the defining indicator within the two groups of interest will be the specific origin of manufacture. The two groups will then consist of manufactured items manufactured within the United States and those imported.

Statement of Hypothesis

In this study the following null hypotheses are examined at an alpha level of .05. A one-way ANOVA is to be used to compare groups as to whether a significant difference exists between the two means of the associated groups. In this study, the two groups will consist of 102 random samples of manufactured items intended for consumption or close oral contact by a child six years old or younger or infants. The groups compared will be 51 items that were manufactured in a country other than the United States and 51 that are as close a match as is possible, described as “best fit” to the items found, however, manufactured in the United States.

H_0 There is no significant level of any elemental toxin detected in any sample tested from sample groups of products.

H_{01} There is no significant level of elemental toxins detected in products that were manufactured in the United States but significant levels of elemental toxins will be detected in products manufactured in countries other than the United States.

H_{02} There is no significant level of elemental toxins detected in products manufactured in countries other than the United States, but significant levels of elemental toxins will be detected in products manufactured in the United States.

H_{03} There is no significant level of mercury found in any sample tested, but other elemental toxins will be detected at significant levels, specifically, lead and bromine.

Outline of Work

This analysis of manufactured products requires the purchase of random products for use in this study. Purchases will start in June of 2007 and continue through January 30th of 2009. This will allow 20 months to elapse, during which the researcher may shop for and purchase the 204 items needed to complete the study. Only 102 items, 51 manufactured outside of the United States and 51 manufactured in the United States and the best matches possible, will eventually be analyzed. Another 102 items will be identical, purchased at the same time in the same store and used as a control measure and part of the random assignment of items to be tested. All items must meet the following requirements to be considered for this analysis:

1. They must be manufactured. This will be defined as constructed from multiple components to assemble a non-naturally occurring product.
2. All products will be considered to have a high percentage of reasonable usage by children aged six and younger.

3. Any product chosen must have two of the identical product available for purchase as one will serve as the control in a random selection.
4. All products must be sealed in packaging whose label indicated contents and country of origin.
5. All items must be edible or specifically made to come in close oral contact with a child six years old or younger.
6. Some but not all of the parameters for selection of items will be brightly colored wrappers with cartoon or animal drawings that specifically target young children. Some economy packaging might not have this format, but the item may still be suited to study.
7. Items must fall within reasonable cost limits for this analysis, set at a maximum of $15.00, for each sample of two identical items.
8. Over the 20-month period of time specified, the researcher will randomly purchase items that fit all criteria and can be stored sealed in their original containers.
9. All items will be stored in large plastic containers to ensure reasonable secure storage and freedom from crushing and exposure to the environment.
10. Upon completion of the research proposal by all members of the committee, the researcher will take items sealed to the Physical Science building on the campus of Oklahoma State University.
11. Each individual pair of manufactured items will be removed from the large container and a coin flipped to determine which will be analyzed. The item not analyzed will be kept sealed and serve as a control in this study. Items will be

randomly marked with a capitol letter A or B before the coin is tossed and "Heads" will signify that sample A will be analyzed while "Tails" will signify sample B will be analyzed.

12. Items will only be handled with gloves and only opened inside the chemistry lab room on the third floor of the physical science building at Oklahoma State University.
13. Samples in the liquid phase were massed on a tare with a scale whose accuracy is +/- .0000 grams. A sample that fits into the wells in the (XRF) will be procured in this manner.
14. Some items might not brittle enough for the researcher to break in this manner and, in addition, size-prohibitive for measuring in the (XRF) wells. Every attempt will be made to control variables such as measurement devices for analysis. These items that prove resistant will be analyzed using the hand held Niton (XRF).
15. All analyses that show significant findings will be carefully saved in the form of a print out of the (XRF).
16. Before analysis takes place, a spread sheet will be prepared, placed on a clip board, and taken into the (XRF) room on the 3rd floor of the Physical Science building at Oklahoma State University.
17. As each sample is read by the (XRF), the spread sheet will be carefully filled in; recording levels of elemental toxins found additionally all values are saved by the computer attached to the XRF.

18. Any item that tests for elemental toxins above those allowed as published by EPA standards or Ellenhorn (1997) for that toxin, will be compared to 5SD above the mean for standards prepared of each toxin to facilitate overcoming as much as is possible the matrix effect and to strive for accuracy.
19. Levels of toxins established as significant will be 125 ppm for bromine, 1 ppm for mercury and .1 ppm for lead if found to be contained within any sample. These levels have been chosen based on direct quotations from reliable sources described within the methods section of this research.
20. In addition, any item that tests for elemental toxins above those allowed as published by EPA standards or Ellenhorn (1997) for that toxin will be analyzed a fourth time by use of the hand held Niton (XRF) .
21. A series of trials will be run each day in the study. At the completion of each day's trials, Dr. Apblett, serving as advisor on this researcher's committee, will be invited to double-check all values recorded by this researcher to further verify their accuracy if significant levels of a toxin are found in a sample. In this way, the same sample contaminates will be verified by an accepted expert in the field of (XRF) technology.
22. All items will be carefully saved and those opened for analysis will be stored by sealing in zip-lock bags to preserve their integrity. Both the analyzed items will then be sealed back into their original zip-lock bag that was labeled with their designated number and initials.
23. Items manufactured in the United States will be sequentially and randomly labeled with a marker on the zip lock bags as: U.S.1 A, U.S.1B, and U.S.2 A,

U.S.2 B, In addition, items manufactured in countries other than the United States will also be randomly labeled as O.C.1A, O.C.1B and O.C.2A, O.C.2B with O.C. used as an abbreviation for the words “other country”.

24. All readings will be compared and averaged as part of the data presented in this research.
25. A one-way ANOVA will be conducted, comparing the two groups with a 0.05 alpha for all hypotheses.

CHAPTER II

REVIEW OF LITERATURE

The Elemental Toxin Lead

Toxic elements occur quite commonly in locations where, throughout recorded history, according to Nriagu (1983), humans have accidentally been poisoned. One such toxic element Nriagu discussed is the common metal lead. For thousands of years, lead held a wide variety of uses, with one of the more interesting as a valued sweetener. Historically, honey was the only readily available sweetener until the discovery of what was called sugar of lead. Nriagu (1983) stated that lead containers were in common use by ancient peoples due to the fact that this toxic metal was readily available and very malleable.

Early alchemy, Nriagu (1983) reported, was conducted by introducing unfermented grape juice into such a container, and heating it, thereby condensing the juice into viscous syrup. This sweet, poisonous substance was called defrutum or sapa. These terms, along with other ancient terms and proper names common within languages thousands of years ago, have no modern translation and so might appear difficult but they are included in order to portray more concisely the different lead-laden concoctions produced. Nriagu (1983) explained that defrutum or sapa was poured from lead containers and added to many food stuffs, to enhance taste. Nriagu stated that wide spread use of this sweet boiled down grape syrup was most commonly used to enhance

soured wine. The ancient writings that describe the production of defrutum and sapa are specific in that it must be slowly simmered in a pot made from lead. Nriagu (1983) further explained that this process resulted in the early alchemy of producing what was termed “sugar of lead.”

When organic sugars from the grapes juice were breaking down during fermentation to form acetic acids the resultant acid would react with the lead pot to form crystals of lead acetate. This white crystal looking much like modern refined sugar became the Romans preferred sweetener.

Some modern chemists according to Nriagu (1983) have tried to follow ancient and precise recorded directions and have reenacted the recipes for defrutum or sapa. These attempts have produced lead concentrations with up to 1000 mg per liter of lead in this sweet and preferred potion. Sapa was boiled for a longer period of time than defrutum causing it to become more viscous but the basic chemistry was identical. Nriagu (1983) also reveals that large numbers of lead pots used for cooking have been recovered from the ruins of the Roman civilization in various areas of the empire (p.660-661).

Ancient peoples, reported Lewis (1985), also made some coinage using lead which, when handled, could easily transfer to hands and other surfaces as lead is a very soft metal. Ancient cultures also decorated their buildings and themselves with paints, dyes, and makeup and these ascetic mixtures were frequently concocted with lead as a key component. Lewis, (1985) stated that this practice inevitably contributed to the common metal, lead, being transferred from art to the internal workings of the human body. Lewis quoted on a website (1985) reported that lead was considered to be the patriarch of all of the metals. It also served according to Lewis (1985), as an early form

of birth control due to lead's detrimental effect on sperm. The plates, pots and pans and saucers of many ancient households were made from pewter, a silvery alloy, mixed with lead that inevitably passed though in continual tiny amounts into many acidic food stuffs served on this lovely but poisonous dish ware.

According to Lewis (1985) ignorance of lead's poisoning effects and its natural abundance made its use economically and socially acceptable. Only within the last fifty years has the realization of lead's omnipresent danger dawned. According to Lewis, this realization resulted in statements made by the EPA's first administrator concerning potential problems. Lewis (1985) stated quoting the EPA's administrator, William D. Ruckelshaus, "An extensive body of information exists which indicates that the addition of alkylead to gasoline results in lead particles that pose a threat to human health." Lewis was referring to the lead additive that was used as an anti knock agent in most blends of gasoline and whose usage still prevails in many developing countries today.

The United States medical community established through multiple studies as reported by Silverman and Fodera (2007) that the population at higher risk for lead poisoning and long-term effects consists of children six and younger including toddlers and infants. Silverman and Fodera quoted in an online document (2007) found the following:

> The greatest risk of injury from lead poisoning is to children under the age of seven, whose developing bodies and brains are sensitive to even small amounts of lead, which can leave children with irreversible injury that does not appear until many years after the exposure to lead. The kinds of injuries lead causes in children include: learning disabilities, brain damage (sometimes subtle), loss of IQ points and intellect, academic failure, neuropsychological deficits, attention deficit disorder, hyperactive behavior, antisocial (criminal) behavior, neurological problems, encephalopathy (brain swelling), major organ failure, coma, death. The United States Centers for Disease Control and Prevention in Atlanta (CDC) has concluded that the risk of a child's suffering the above injuries begins when a

> child's blood-lead level rises to a mere 10 micrograms per deciliter of whole blood. And while lead poisoning is treatable in the sense that there are medical and environmental interventions that can prevent further lead ingestion and help a child to excrete the lead that has already been ingested, the damage that lead does in a child's body is not treatable: once any lead is ingested, the damage is done and is permanent.

Even though lead has been used by humans for multiple purposes throughout history, the human body as reported in the web based journal, *Living on Earth* (2007), has no required concentration of lead within any anatomical system who stated: "Lead is what scientists call xenobiotic, a foreign substance with no useful role in human physiology, toxic even in minute quantities."

All forms and compounds of lead, according to Perez (2008) are poisonous to humans. But the most common, bivalent lead serves as a poison when the body mistakes it for calcium, which is vital for the functioning of many organs and systems in the human body. The medical community, as updated by Perez for the U.S. National Library of Medicine, concluded that the effects of lead poisoning are profound. Perez elucidated that lead is a very real danger to human beings, especially small children and infants with whom even greater care must be taken to avoid contamination. Perez (2008) updated and reported online that lead is a very strong poison that most typically builds up slowly over time. This happens when there are repeated microscopic exposures to this common metal. Perez (2008) specifically focused on leads effect on small children stating it is more harmful to this segment of the population due to their developing nervous systems and brains. He further elucidates that the younger the child the more harmful lead poisoning may be and that the unborn fetuses are most at risk. Children are also more at risk due to their behaviors of putting everything in their mouth as these actions might facilitate lead poisoning from any object of food containing lead. Perez (2008) explained that tiny

amounts of lead can literally be inhaled when in the surrounding atmosphere. He stated that tests have shown that many children have levels that exceed acceptable limits of lead in their bodies. Any child could be exposed however prevailing research at this time points toward those children living in older homes where pealing lead paint serves as the main avenue of contamination.

Appleton (2000) discussed lead poisoning effects which have occurred in about every part of the human body including the brain, kidneys and blood, and stated that lead is especially damaging to the developing skeletal system where lead is mistaken by the body for calcium. Appleton explained that when new cells grow within a medium contaminated with lead, the body mistakes lead for calcium and attempts to deposit it in bone, teeth, blood or other systems of the body where calcium serves a vital function. When one replaces the other, biological structures cannot function correctly and the resulting symptoms are referred to as lead poisoning. Sadly, until detected, as reported online by Appleton (2000), many people might spend a lifetime being slowly poisoned from lead laden contaminates in their environment, demonstrating all of the symptoms of lead poisoning and never being diagnosed as having lead poisoning. Appleton on a website (2000) stated that the main source of lead in an adult in North America is their own skeleton. After a lifetime of continual exposures when the body mistakes lead for calcium it hides within the bones of the body. Many scientists are now advocating that all adults take a hefty dosage of a calcium supplement daily. Appleton (2000) explained that as many people age they consume less calcium rich foods and this sets into motion the cycle where the body not supplied with enough of the vital element calcium will compensate by cannibalizing it from the skeleton. According to Appleton, with lead

hiding within adult skeletons masquerading as calcium, many older American can find themselves with too much free lead in their blood. When this aforementioned cycle occurs, it causes havoc within important anatomical systems.

In the United States, routine blood tests are commonly conducted during a well child check up reported Nadakavukaren (2006). Levels of lead are measured in the blood, and these levels, abbreviated (BLL) for blood lead level, are established as a standard to measure amounts of this toxic element within a child's body. Nadakavukaren, as reported on a website (2006), stated that lead even at low levels can be very devastating to small children. She explains that once the damage from lead poisoning occurs it can never be completely reversed. With this in mind she stated that prevention of lead exposure should become a focus in this society.

Nadakavukaren (2006) further explained that edible products have recently surfaced which, when tested, show high levels of lead resulting in lead poisonings. Nadakavukaren (2006) delineates that some of these edible items are being imported from countries other than the United States. Nadakavukaren on the same website (2006) reported that salty snacks imported from Mexico called "chapulines" were found to be contaminated with high levels of lead. In addition some cases of severe lead poisoning have occurred when people in the United States as reported by Nadakavukaren, used an imported product from the Dominican Republic called "litargirio." One brand of "litargirio" tested by authorities in the state of Rhode Island was found to contain 79% lead.

Currently, reported the online Mayo Clinic, children suffering from more severe levels of lead poisoning are given chelation drugs. The chelation process, slowly and very

painfully, will remove lead from the patient's body. In conjunction with chelation, the blood lead level (BLL) is periodically taken as a measurement of the remaining lead. Mayo Clinic staff, (2006) states that in "more severe cases, your doctor may recommend treatment called chelation therapy in addition to removal from lead exposure. In chelation therapy, the medicine (chelating agent) administered binds with the lead resulting in it being excreted in urine."

Research reported by Segelken in an online document (1999) indicates that chelation therapy might also remove zinc along with lead. When the chelation agent is added, it might chemically bind to any bivalent element and cannot discriminate between those that are toxic and those that are vital to life. Another common bivalent metal discussed by Segelken (1999) is zinc, which is critical to a healthy immune system. Segelken (1999) discussed that the most common drug used in chelation therapy Meso-2, 3-dimercaptosuc-cinic (DMSA), also known as succimer might also bind to and leach out zinc from the body. Zinc like lead and calcium has two valence electrons and the human body confuses these metals as they are deposited for various vital functions. Zinc is essential for immune system functioning and this might explain, stated Segelken(1999), why many children who have endured the pain of chelation show problematic side effects within their immune systems. Segelken (1999) also elucidated that in some cases lead poisoning itself enhanced certain immune responses associated with allergies and asthma.

Canfield et al. (2003) reported that while there have been declines in blood lead levels over recent years, little research has been conducted on low levels of this elemental toxin in small children. As reported on a website, Canfield et al. (2003) conducted research on levels of lead in small children and correlated these levels with specific

intelligence tests. Canfield et al. reported that in this study, children with a blood lead level below 10 ug per deciliter (0.483 nmols per liter), little work has been to ascertain the neurobehavioral implications of small amounts of lead being ingested. Canfield et al. (2003) explains that within this research 172 children at 6 month intervals were measured for lead blood levels. The Stanford-Binet Intelligence Scale was administrated to these children at 3 and 5 years of age. All potential cofounders were adjusted for such as maternal IQ and the quality of home life. In conclusion, Canfield et al. reported that the blood lead level was inversely and significantly associated with the child's IQ. The resultant findings of this study explained that for each increase of only 10 ug per deciliter of in the lifetime average of lead in the childes blood there was an association with a 4.6 decrease in IQ.

Canfield et al. (2003), on the same website, concluded this important research with the following call to tighten the initial exposure of children to lead as opposed to just treating poisonings after they occur, stating that the findings of this research show considerably more children in the United States are exposed to lead that has been currently estimated. This research stated that there is no truly effective treatment for lead poisoning when even moderate levels are detected.

Perhaps the most widely quoted authority on toxicity is *Ellenhorn's Medical Toxicology*, (1997), a text in which numerous elemental toxins are defined and described as a reference for physicians. Ellenhorn devotes numerous pages with many citations from rigorous scientific studies to the effects of lead poisoning especially on small children and infants. Ellenhorn (1997) reported that low levels of lead may cause neurological impairment, decrease of IQ, or behavioral and learning disorders in children.

Ellenhorn further states that even low levels of lead contribute to deficits in motor functions and cognitive decline. Data from numerous studies indicates that there is a decrease in IQ points when children have been exposed to lead. The most critical time frame, Ellenhorn reported in a young child's life, is the range from 15 months to four years of age. Based on multiple studies and their associated data along with Ellenhorn's conclusions, the Centers for Disease Control subsequently lowered the definition of childhood lead poisoning from, "1.21 to 0.48 umol/L (25 to 10 ug/dL)." Ellenhorn concludes the discussion of lead poisoning stating that there is no safe level of lead and "a threshold where there is no influence on children cannot be determined at this time."

It has been estimated by Salazar (2007) that currently many tainted products are entering the United States and, Salazar further states, the only reaction to these tainted products is to block their import after these items have already been purchased and exposure has occurred. Salazar, as reported on a website (2007), explained that there are approximately three hundred billion dollars worth of Chinese made products entering the United States each year. Currently, Salazar (2007) explained the official United States policy is that when a tainted product is found the action by the government is to block its import and recall that specific product. Salazar also notes that the United States government has confirmed tainted products imported from multiple countries, China is noted as the largest offender however Mexico and India and other countries have also produced these products that have been found to not meet United States standards for lead content.

Recent years have seen a dramatic increase, reported online by Lum and Nanto, (2007) of imported goods into the United States facilitating a huge shift in the

manufactured products system in this country. According to an online document by, Lum and Nanto, (2007) China currently has a huge trade surplus with three major areas – the United States, the European Union, and Japan. As recent as the year 2005, the United States alone has increased its trade deficit with China about 25 % from the previous year. In the year 2003 China overtook Mexico as the second largest imported of products to the United States.

Research has found, reported Adebamowo (2007) for the University of Cincinnati in their online format, that some companies might even be making multiple products for export to different countries depending on the environmental regulation within each for lead content. A group of researchers, under Adebamowo at the University of Cincinnati, also reported that once toxic substances have been detected, a recall will be ordered; however the public is still at risk for poisoning while the slow spread of this recall potentially reaches the consuming public. Adebamowo (2007) reported online for the University of Cincinnati that the University of Ibadan analyzed lead levels in five different colors of paint, from five different brands of paint each sold in Ibadan. Ibadan is a city of 2 million people in Nigeria, Africa. The results of this study showed that 96% of the paint available for sale in this area contained higher than recommended levels of lead. It was noted that especially the bright colors of yellow, red and green were found to have the highest lead content when compared to white paint. Adebamowo, worked collaboratively with other research previous published in the journal *Environmental Research* which had also studied lead levels in paint. This study by Adebamowo measured lead levels in paint from India, Malaysia and China and found that all exceeded United States regulations. One of the coauthors within this Adebamowo

study, reported that one paint manufacturer sold low level lead paint to Singapore when a shipment of paint was ordered as this country has strict regulations on lead content; however the same paint factory sold paint very high in lead to countries with little regulation.

Woolf and Woolf (2005) stated that spices used to enhance food items' flavor may be found to be high in lead. While most cases of lead poisoning are from contact with lead based paint or dust in the air from lead paint of lead products there are other sources. Woolf and Woolf explained that these products are for the most part sold in countries other than the United States and the purchaser was free to travel back to the United States then used the spices in food preparation, resulting in lead poisoning. Woolf and Woolf on a website (2005) reports that two families had children that were poisoned by lead contained in spices. One of the spices was purchased in the Republic of Georgia and is called swanuri marili. When analyzed this traditional spice of this region was found to contain "100 to 2040 mg/kg of lead content" The second family involved had purchased spices while traveling in India. The spice in question here was called "kozhambu" shown when analyzed to have a lead content of 310 mg/kg. Woolf and Woolf described process of chelation that the young children in both families under went to facilitate lead removal. Woolf and Woolf concluded by issuing a warning that lead laced paint is not the only way a young child can be poisoned by this metal. The question Woolf raised of exotic spices laced with lead raises the question of food stuffs imported from various countries seasoned with exotic and potentially lead laced spices.

An avenue other than food products that could potentially allow lead poisoning to occur is through contaminated waters in United States reports, The Center for Hazardous

Substance Research (2008) in discussing Superfund sites and the problems they pose. One such published Superfund site report by The Center for Hazardous Substance Research is surrounding a former lead mine in southeast Kansas. The Center for Hazardous Substance Research further elaborates that lead was mined in this central location which is surrounded by many natural water systems above and below the ground. For over a century these water ways have provided for possible transport of this elemental toxin. The Center for Hazardous Substance Research was quoted online (2008) reporting that for over a century lead was mined in what is called the Tri-State region located in southeast Kansas. This has resulted in over 3000 abandoned mine shafts and numerous environmental hazards in the area. Waste mine tailings, also called chat, litter the area in open, wind swept piles. In addition leaching of fine metal-dust from runoff moves contaminants in to nearby streams and into river systems. When these lead mines were abandoned, many filled with water and they began contamination of local aquifers and surface waters.

The Center for Hazardous Substance Research (2008) also reported that the EPA has established clean-up efforts in many areas of this region. The question that lingers is whether elemental toxins are finding their way into local waters and still posing environmental and public health risks. The Center for Hazardous Substance Research in an online document refers to the present-day conditions; for example, tailings left by the mining process and collapsed mine shafts exposing the surface to elemental contaminates. As reported on a website by, The Center for Hazardous Substance Research (2008) the cleanup efforts in this area were extensive. They report that surface

waters were redirected and many surface mine tailings were buried. They also reported that currently problems with this abandoned lead mine system still persist.

As reported online by, Basic Information, What is Super Fund. (2007) many areas currently called Superfund Sites are evident in multiple locations. These online documents refer to the dynamic and erosive nature of water as a universal solvent facilitating multiple toxic elements finding their way in water systems. The Environmental Protection Agency (EPA) reported in these documents that it has identified 1,228 different Superfund sites within the United States. The (EPA) website, Basic Information What is Super Fund (2007) stated that "Superfund is the name given to the environmental program established to address abandoned hazardous waste sites." This falls under the fund established by the "Comprehensive Environmental Response, Compensation and Liability Act of 1980, amended (CERCLA)."This act allows the EPA to clean up such sites and to hunt for the responsible parties for government reimbursement if possible.

The United States Geological Survey (USGS), Industrial Water Use (2005) states manufactured products use large amounts of water in their production lines to format their specifically desired end product for public sales. The following quotation, along with reports which concern potential contaminated waters leaching from Superfund sites, should serve to clarify the method by which contaminates including lead, might find a potential avenue to enter manufactured products. The USGS website, Industrial Water Use (2005), updated and reported that every manufactured product used water during some part of the production process. Water may be used for fabricating, diluting, cooling,

washing of incorporated within a product. The companies that use very large amounts of water in their products include manufactured food products.

The Elemental Toxin Bromine

Korslin (2003) discussed another elemental toxin, bromine, which is commonly found in sea water. This elemental toxin becomes a very poisonous substance if ingested in sufficient quantities, especially by infants and small children. Element 35, bromine is a member of the halogen family that has many uses, among them as discussed by Korslin, is its use in tiny amounts, usually parts per million (ppm) as a disinfectant similar to the addition of chlorine to water systems as a bactericide. According to Korslin, bromine used in this manner had been largely isolated to conditions where chlorine's usage is not appropriate. An example of this would be on large ships at sea or areas where chlorine's volatile nature as a gas is not deemed safe or appropriate. Korslin (2003), quoted on a website, explains that while bromine was known to be a toxic substance, it could be used in tiny amounts to kill bacteria, thus making waters safe to drink and explained that at the present time only two halogens, chlorine and bromine are approved by the EPA as disinfecting agents for shipboard potable water. While chlorine has established dominance in land based application, its reactive and corrosive nature as a gas at standard temperature and pressure poised problematic feasibility on a ship. Korslin reported that chlorine had directly facilitated several onboard fires and therefore bromine usage was deemed a likely substitute. It was further elucidated that the viable usage of bromine in this manner was not possible until the year 1957. Korslin explained that the Dow Chemical Corp. created a brominated ion exchange resin for this purpose. Currently

polybromide resins sealed in cartridges are widely in use in potable water systems on board ships and oil well exploratory stations.

In addition, due to some bromine compounds ability to kill anything living in the soil, bromine compounds are thought to insure better crop yield when applied to agricultural areas. The United States Environmental Protection Agency (EPA) set clear limits on the uses of known toxins, including bromine, when they reported on the website, What the Pesticide Residue Limits are on Food: EPA (2008), with residues set in tiny increments to ensure public safety. What the Pesticide Residues are on Food: EPA (2008) reported the following:

> 180.519 Bromide ion and residual bromine; tolerances for residues. (a) General. The food additives, bromide ion and residual bromine, may be present in potable water in accordance with the following condition: (1) The food additives are present as the result of treating water aboard ships with a polybrominated ion-exchange resin (as a source of bromide) under the supervision of trained personnel. (2) Residual bromine levels are controlled to not exceed 1.0 parts per million (ppm) in the final treated water. Control is effective using calibrated or recirculation or proportioning bromine feeder equipment and periodic checks of residual bromine using a bromine test kit. 180.521 (3) Residues of inorganic bromides (calculated as Br) in milled fractions derived from cereal grain from all fumigation sources, including fumigation of grain mill machinery, shall not exceed 125 parts per million" US EPA Pesticides and Food: What the Pesticide Residue Limits are[sic] on Food.

Poelarends et al. (1999) discussed that while the Environmental Protection Agency had set strict limits on this toxic elemental poison, in published reports, the same agency acknowledged that some compounds containing bromine are hazardous to the extent of having been classified as a carcinogen and mutagen. Poelarends et al. explained that in 1983 the EPA banned the use of a fumigant called Ethylene dibromide (EDB) which is also known as 1, 2-Dibromoethane. This fumigant was widely used to prepare acreage for planting under the theory that, if all biological activity including fungus and

insects were eliminated, plant growth would be enhanced. As delineated by Poelarends et al. (1999), this toxic substance is still being produced and used in some countries and has become a possible contaminate in the United States water supply as it does not readily break down and therefore continues to be slowly released over time. Poelarends et al., quoted on a website (1999), explained that "1, 2-Dibromoethane is a man made organic chemical that was at one time used as an antiknock additive to certain types of gasoline". In addition it has been widely used as a pesticide on soils to enhance crop production. Poelarends et al. stated that 1, 2-dibromoethane has been shown to have cancer causing potential and with runoff into ground waters being detected declines of its usage in some countries has reduced exposure to this extremely toxic xenobiotic.

The problem this report states, is that this known carcinogen is still produced and used in several countries. Poelarends et al. (1999) explained that this bromine containing chemical, 1, 2-dibromoethane is utilized as a lead scavenger, a fumigant for stored grain and an intermediate in some dyes and pharmaceuticals. Even in countries where it has not been used for many years 1, 2-dibromoethane is found in what Poelarends et al. called "remarkably high concentrations because it reacts with the soil matrix." 1, 2-dibromoethene which contains the bromine ion is still a continuous source of contamination within many water supplies world wide.

Pollan (2008) explained that healthy soils contain a complex mixture of biological activity. This includes fungi that are in a symbiotic relationship with many plants. Biologically active soils are an integral and dynamic part of any healthy ecosystem and, as reported by Pollan (2008), a lack of fungi in these healthy soils creates less nutritious crops citing considerable amounts of research concluded that crop plants grown with

industrial chemicals tend to be often nutritionally inferior to those grown in organic soils. He explains that there are several probable hypotheses for this variation, one of which is that, with chemical enhancements, crops grow with more speed giving the plant less time to accumulate nutrients. In addition biological activity in the soils plays a dominant role in nutrient levels of crops as slow decomposition of organic matter releases a wide range of plant nutrients. Pollan (2008) delineates that in healthy soils the natural fungi mycorrhizae, live in a tightly woven symbiotic relationship with the roots of plants. The trade involved in this symbiotic dance is a supply of necessary minerals and metals given to the plant with which it can build vitamins and nutrients, traded for a ration of sugars for the fungi from the photosynthesizing plant.

The United States government estimates according to the Center for Disease Control, CDC Home (1992) on the wide spread use of 1, 2-Dibromoethane which served to deliver bromine as an elemental contaminate are astounding. Even with a current ban in the United States, other countries which the United States imports products from still allow the use of this toxin. Describing the method by which poisonings may have occurred, the CDC Home (1992) on their website stated that the most common source for human exposure is from ground water where this toxin may be slowly leached many years after its prescribed usage has ceased.

Many soils contain tiny clump like structures called micropores. If these micropores are crushed or disturbed the 1, 2-dibromoethane can be released into the surrounding ground waters. The CDC Home (1992) explained that this xenobiotic chemical persists in soils and in ground water for long periods after the initial usage. This government watch dog agency, the CDC Home, stated that the most likely avenue of

ingestion of 1, 2-digromoethane was in drinking water or the products that used drinking water in their manufacture.

Within the same website, the CDC Home (1992) goes on to explain that residue from this known carcinogen has been found in food and other commodities and could potentially persist for years to come. The CDC Home (1992) reported with 1, 2-dibromoethanes stability in water systems they expect it to persist for years in ground water. The CDC Home also reported that in the past this toxin was used as a gasoline additive and widely utilized as a crop fumigant. It has been detected in the air, soil, ground water and in many food stuffs due to its stable nature.

Reported by Letz et al. (1984) in the online Journal of the American Medical Association (JAMA), even small residues left over from manufacturing a deadly toxic substance containing bromine can prove fatal if encountered within in a confined area. Lenz et al. discussed that during the decades when the United States allowed the manufacture of the bromine ion containing product, ethylene dibromide, it had just this effect on an employee who was instructed to clean a small area containing a minute residue of this designated carcinogen. As reported by Letz et al. in the online JAMA (1984), ethylene bromine caused a worker to die within 12 hours of exposure in an enclosed space. Some chemicals that contain bromine such as ethylene bromine are extreme hazards to human health.

The U.S. Environmental Protection Agency (2007) has reported that new regulations within the last decade set up a more careful monitoring system for pesticide residue, especially in manufactured items that might be consumed by children. In 1996 a

new attempt was made to control these residues in food stuffs as reported on the website for, The U. S. Environmental Protection Agency (2007):

> In August 1996, the Federal Food, Drug, and Cosmetic Act was amended to include the Food Quality Protection Act or FQPA. This Act required EPA to reassess by August 2006 all of the pesticide tolerances that were in place in early August 1996 to ensure that they met current safety standards and was supported by up-to-date scientific data. FQPA requires EPA to consider risks to infants and children when setting tolerance. In accordance with FQPA, all tolerance decisions take into account the special susceptibility of children to pesticides. EPA has cancelled use of several OP pesticides on many "kid" foods, such as apples, and utilizes an additional tenfold (10X) safety factor as appropriate in setting and reassessing tolerances. Children are at a greater risk for some pesticides for a number of reasons. Children's internal organs are still developing and maturing and their enzymatic, metabolic, and immune systems may provide less natural protection than those of an adult. There are "critical periods" in human development when exposure to a toxin can permanently alter the way an individual's biological system operates.

Manö and Andreae (1994) reported in the online journal *Science*, that the most probable source for methyl bromides' increase as a source of bromine is anthropogenic in nature. This journal article clarified that bromine as a salt ion naturally occurs in ocean water in small amounts. These tiny amounts and their containment within a dynamic liquid environment prompted Manö and Andreae and other researchers to look for more probable sources of the increased amount of bromine currently found to be open to bioavailability. Manö and Andreae (1994) reported online that human activity has dramatically increased the significance sources of bromine containing compounds globally. Anthropogenic sources vary with many different compounds containing bromine but as a whole this elemental toxin that was once almost exclusively found in ocean waters or dehydrated ocean salts has become a global concern in some of its more toxic compounds or forms. Manö and Andreae (1994) reported that the Montreal

Protocol added an amendment to their global concerns and called for a "January 1, 1995 freeze in methyl bromine production at 1991 levels (p.1255).

Methyl Bromide, a compound that contains the element bromine, is considered to be very volatile in nature and as reported by the EPA (2008) on a website called "Methyl Bromide Questions and Answers" is assumed to be given off into the surrounding air. Growers will try to forestall this according to the EPA by using multiple methods. The EPA (2008), in Methyl Bromide Questions and Answers, an online website, reported that when it is injected into the soil it will effectively sterilize the soil killing the majority of all types of soil organisms. Immediately after this bromine containing chemical in injected into the soil, the planted area is covered with large plastic tarps. This tends to slow the release of this fumigant into the atmosphere. This is generally the case with strawberry production in the state of California. In Florida the tarps are left on the crops the entire growing season. About 50-95% of this Methyl Bromide typically reenters the atmosphere. The EPA reported that the other main crops that commonly use this toxin include peppers, grapes, nuts and many vine crops.

Some research as reported by the British website publication, The International Program on Chemical Safety (1999), has indicated that Methyl Bromide might have a far longer life when it is held within the soil structures and within food items if contained or encapsulated in a form to inhibit vaporization than within the plant being harvested. While this was reported to be uncommon by, The International Program on Chemical Safety, they stated that levels above those found naturally in the oceans are reported near where Methyl Bromide has been in use. The exact amount of bromine naturally found in the ocean and a comparison of that amount to the current levels has been reported online.

The International Program on Chemical Safety (1999) reported on their website that the natural levels of Methyl Bromide found in ocean water is typically given as 140mg/L and the average value of this same compound in samples taken from the North Sea was 18.4 mg/L. Inland waters contain much lower amounts naturally except in regions where fumigation with Methyl Bromide was practiced. In drainage waters from a Netherlands greenhouse 9.3 mg/L Methyl Bromide and 72 mg/L of the bromine ion were reported. In Belgium, the water discharge from another greenhouse was measured to have 280 mg/L of bromine ions after fumigation had occurred. This is twice the normal amount found in sea water. International Program on Chemical Safety (1999) in their report stated that levels of Methyl Bromide or the element bromine may be elevated in foods that have been grown on soils treated with Methyl Bromide. Fresh vegetables have been observed to exceed the permitted levels of this toxin. In some countries, concerns have prompted legislations prohibiting the growth of vegetables on treated soils.

Disse et al. (1996) was quoted on a website and reported that another possible ionic compound containing bromine that may have caused serious health risks is sodium bromide. Results of experimentation showed that rats given this compound had suffered significant detrimental effects explaining that bromine ions interfere with interactions of neurons in adult rats. Disse et al. (1996) further announced that bromine may affect the neuroplasticity of the brain during postnatal development. This research describes rat embryos exposed to sodium bromide (NaBr) by providing an aqueous solution containing a very small percentage of NaBr to the pregnant dams. The pregnant rats were only given these solutions from the 5^{th} to the 15^{th} day of gestation. The control rats in this experiment were given tap water with a small similar percentage of NaCl to drink. A

measurement of the bromine transfer to embryos was made from samples of blood and brain tissue. Even with the availability of the NaBr solution stopped before birth of the baby rats, the dams excreted bromine in their milk fed to their young up to 10 days after birth. Significant and permanent delays in postnatal development were observed in all of the bromine –treated animals. These included, Disse et al. reported, body weight, brain weight, and the protein content of the brain. Also there were some changes of certain brain structures; for example, the laminar structure of the neocortex was altered. The conclusion of this research stated that exposure to moderate levels of NaBr may interfere with postnatal development deficits that include the brain of rats. The author notes that the exact mechanisms by which bromine ions cause these deficits remains unclear and more research should be undertaken.

According to Golomb (1999), when a bromine ion has been taken into the human body, very little is understood about the complex interactions that take place. Furthermore, she stated, while bromine may be found in many ionic compounds, any of these in too great of a quantity may result in acute poisoning called bromism. As reported by Golomb as quoted on a website, this is due to the interaction between bromine and the vital ion chlorine as bromine tended to replace chlorine in the human body, disrupting many vital biological systems. Golomb reported that currently the medical community assumes that bromine acts to replace chlorine in the body. She adds that even though bromine has been used in various medical treatments for more than a hundred years little is known about the action of bromine at the cellular level. The guess is that the introduction of this ion may interfere with synaptic processes by substitution for chlorine ions in the actions of neurotransmitters. A specific example of this interference is cited by

Golomb is that of GABA, or gamma amino butyric acid, the chief inhibitory neurotransmitter in the brain. This neurotransmitter functions with specialized chlorine ion channels. In addition it was suggested that in some regions of the brain, blood flow may be altered and that resultant symptoms of this shift are referred to as bromism. Golomb cites research where cerebral blood flow was assessed in a case study involving bromine psychosis where the blood bromine level was found to be 45 mEq/L considered to be very high and in the deadly range. The cerebral blood flow of the person referenced in this study was found to be only one-third of normal blood flow. This included blood flow to such important areas of the brain as the frontal and parieto-occipital areas. Golomb concludes stating that changes in regions of the brain blood flow and neuronal activity changes directly relate to symptoms of bromine poisoning called bromism.

Golomb (1999) quoted on the same website also described the different toxic levels of bromine when found in the human body and displayed a chart listing symptoms at each level. She referred to this published chart as a reference to define different levels of bromism as accepted by leading authorities.

Table 1

Bromide[sic] Blood Concentration and Toxicity

mg/dL	mEq/L = mmol/L	Toxicity
< 50	< 6.3	"Therapeutic"
50-100	6.3-12.5	Possible toxicity
100-200	12.5-25	Usually serious toxicity
200-300	25-37.5	Possible coma
>300	>37.5	Possibly fatal

Source: Ellenhorn, 1997.

Golomb (1999) devoted an entire chapter in her online text, “A Review of the Current Literature as it Pertains to Gulf War Illnesses”, to the discussion of bromism and its possible implications in regards to human exposures. Many of the reports were very serious in nature and Golomb (1999) wrote on this website that concentrations of bromine in many forms and compounds may have served as a very serious threat to human health explaining that most cases of poisoning by bromine fall into three sub groups, organic bromides, bromoureides, and biotransformation of bromide compounds. She described “organic bromides” as including salts that contain bromine such as potassium, sodium and ammonium bromide. Many of these salts have been used for purported medical uses. These were touted as sleep aids and until the year 1938 bromine salts usage was only surpassed by the use of aspirin in the United States. However during this same time frame many patients that had been admitted to psychiatric institutions were found to be suffering from bromism, not a mental disease. This was a direct result

of the overuse of these common sleep aids. In 1975, all bromine salts were withdrawn from the market for sale. The most widely cited drug that had this profound effect was called Nervine which was made of three different bromine salts and Bromo-Seltzer which contained 3.2 milliequivalents per teaspoon of sodium bromide. Currently with these drugs banned the most likely source of bromine ions is from contamination due to pesticide residue.

In 1996, legislation that limited toxic pesticides in food items was developed by the United States Department of Agriculture (USDA, 1996), under the title "The New Food Quality Protection Act (FQPA)" and signed into law. This legislation noted that foods produced for children and infants were groups within the food supply considered to be a separate and more urgent matter. As reported on their website, The USDA (1996) reported the following:

> A complex piece of legislation, "The New Food Quality Protection Act (FQPA)" reforms the nation's food safety laws. Signed into law by President Clinton on August 3, 1996, the act amends the two major laws involving pesticides: the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) and the Federal Food, Drug, and Cosmetic Act (FFDCA). FQPA revises the FFDCA so that the 1958 Delaney Clause no longer affects pesticides. The Delaney Clause established a zero cancer risk standard for pesticide residues on some processed foods as compared to a negligible risk standard for raw commodities.
> FQPA is important to the methyl bromide issue because many of the potential alternatives to be considered will fall under its provisions.
> Highlights of the new law include…explicitly that pesticide residues be safe for infants and children and includes an additional safety factor of 10-fold, if necessary, to allow for uncertainty in data collected on children's diets. Also takes into account children's special sensitivity to pesticides.

Hotchkiss (1993) reported on a website and explained the history behind the Delaney clause discussed in the new FQPA laws. Within this report, Hotchkiss examined both the positive and negative aspects of legislation surrounding the complex issue of elemental toxins as they pertain to food items. The basic idea of the Delaney clause was

that any chemical that had been shown to cause cancer in animals should not be included in food intended for human consumption. Hotchkiss reported that the Delaney clause passed into law in the 1950's and, given the scientific thinking at that time, seemed a sound idea. The Delaney clause had three basic rationales at its inception. First any substance can be considered a carcinogen if it significantly increases the risk of cancer to laboratory animals when they consume it. Second, a lab animal may serve as a surrogate for humans and data from experiments may be extrapolated to humans. And finally, there is no safe level of any known carcinogenic compound or chemical for humans. In other words, there is no threshold that exists for humans to safely consume a chemical deemed a carcinogen under the Delaney clause.

Schierow (1996) updated an online report for the United States Congress that discussed legislation covering not only the Delaney Clause but the laws that govern the EPA. This report discussed the EPA's role in analyzing manufactured food items for elemental toxins. Schierow (1996) updated and reported on a website that the "104th Congress discussed concerns over a scheduled ban on methyl bromide production. This included the inspection of imported food items for this bromine containing toxin. Congress passed legislation called "P.L.104-170 which provides funding to monitor pesticide residues in domestic and imported food. Congress also directed the EPA to regulate all food under safety standards under the "FFDCA Section 408."

Schierow (1996) further explains on the same websitewebsite, with links to more historical information, that United States laws directed toward the safe use and handling of chemicals that might be used on foods have shifted over the years. Schierow provides a table giving each successive law listed in chronological order with each specific title

and associated number. The complex nature of chemicals used as pesticides and their associated affects on humans receiving small chronic dosages has facilitated a continual shift in the legislation that governs their usage. Schierow (1996) elaborates further supplying details on the same website stating that the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) should regulate all sale and use of pesticides in the United States. There are approximately 21,000 different pesticide products currently in usage. Schierow (1996) included a table showing all legislation that pertained to this area with the year it was passed into law.

Table 2

Federal Insecticide, Fungicide, and Rodenticide Act and Amendments (codified generally as 7 U.S.C. 136-136y)

Year	Act	Public Law Number
1947	Federal Insecticide, Fungicide, and Rodenticide Act	P.L. 80-104
1964	Federal Insecticide, Fungicide, and Rodenticide Act Amendments	P.L. 88-305
1972	Federal Environmental Pesticide Control Act	P.L. 92-516
1975	Federal Insecticide, Fungicide, and Rodenticide Act Extension	P.L. 94-140
1978	Federal Pesticide Act of 1978	P.L. 95-396
1980	Federal Insecticide, Fungicide and Rodenticide Act Amendments	P.L. 96-539
1988	Federal Insecticide, Fungicide, and Rodenticide Amendments of 1988	P.L. 100-532
1990	Food, Agriculture, Conservation, and Trade Act of 1990	P.L. 101-624
1991	Food, Agriculture, Conservation and Trade Amendments of 1991	P.L. 102-237
1996	Food Quality Protection Act of 1996	P.L. 104-170

Source: Schierow (1996).

While the world's agricultural sector and politicians commiserate and struggle with complex interpretations of the usage of bromine containing compounds, Hileman (2004) reported on a website that exemptions to laws have been granted at a United Nations meeting. Even though as discussed previously, on their website, the EPA (2008) had stated bromine containing compounds can be very harmful and their very usage is to sterilize the soil from most of the life therein, some countries have pleaded for the continued use of Methyl Bromide as a pesticide. As Hileman (2004) reported, "On March 26, at a United Nations meeting in Montreal, 114 countries agreed to grant 11 developed countries permission to continue employing the pesticide methyl bromide for so-called critical uses."

Hileman (2004) explained in detail on this website which particular countries and how many metric tons of methyl bromide were exempted at this meeting for what was deemed to be critical to the individual country agricultural system. Hileman (2004) reported online explaining that the "United States will be allowed to use 8,942 metric tons of methyl bromide in 2005. In addition Italy will be allowed the use of 2,133 metric tons; Spain, 1,059; and France, 407." Other countries that insisted on the continual usage of this known toxin as critical for their agricultural interests were Australia, Belgium, Canada, Greece, Japan, Portugal and the United Kingdom who were each granted exemptions for the use of 300 metric tons of methyl bromide." Hileman then clearly describes the rationale for this decision, stating that economic realities overpowered banning of a known carcinogenic substance which is still in common use world wide as the trade off would be less food production in an exponentially growing hungry world.

The Elemental Toxin Mercury

Another elemental toxin of interest is mercury or quick silver as it has been called since ancient times. Scientists, as reported on a website by the University of Wisconsin-Madison (2006), have been concerned that levels of mercury detected world wide might cause harm to people, especially children and small infants. The University of Wisconsin-Madison, (2006) reported that a significant amount of the mercury deposited around many industrial sites was anthropogenic in nature. They stated that there is ample evidence that mercury's health risks were highest to children and women of child bearing years. This report was issued by scientists on the final day of the eighth International Conference on Mercury as a Global Pollutant. The report stated that mercury in the form of methyl mercury has toxic effects especially to a developing fetus.

A concern within the same article elaborated that mining interests were potentially contaminating water supplies with mercury compounds. In the online journal *Science Daily*, The University of Wisconsin-Madison (2006) reported that currently the usage of mercury in small scale gold mining is causing a resurgence of this toxic heavy metal finding its way back into many water systems in regions where people hunt for gold.

Griesbauer (2007), quoted on a website explained that one of the common forms of mercury is the compound Methyl Mercury. This toxic compound is concentrated in living systems as it moves up food chains, potentially being consumed by humans thereby causing a myriad of poisoning associated affects known as Minamata disease. Griesbauer (2007) online described the most severe case of mercury poisoning that has currently been recorded which happened in the small fishing town of Minamata, Japan

during the 1950's. A local plastics company had dumped an estimated 27 tons of mercury into the nearby Minamata Bay. Mercury is used as a catalyst in the production of acetaldehyde, a chemical utilized in plastic production. This dumping created a highly toxic environment with the methyl mercury formed moving up the food chain within the bay from bacteria to plankton to fish and eventually finding its way to people in this area whose main diet was based the local fisheries. Though the process is not understood completely at the cellular level, the basic consensus among scientists currently is that bacteria manufacture Methyl Mercury to rid their single celled bodies of elemental mercury once it has entered their single celled existence from their environment. Once in this form organic mercury easily passes through cell membranes and moves up the food chain.

Eventually in Minamata over 900 people died from mercury poisoning and many children were born with severe congenital birth defects. While Griesbauer explained that this incident was many years ago, it was also noted that among the largest worries concerning current day mercury exposure is China's huge and continually growing use of coal as a fuel source. The burning of coal without sufficient scrubbing of outgases precipitates resultant mercury vapors and is estimated to be the largest anthropogenic source of mercury world wide.

Pottinger et al. (2004) reported for the Wall Street Journal as published on their website in the November 17, 2004 edition, of the omnipresent looming dangers of mercury contamination world wide as he explained that China's coal-fired power plants were releasing the elemental toxin mercury at alarming amounts and rates.

Pottinger et al. (2004) for the Wall Street Journals website reported the following:

> On a recent hazy morning in eastern China, the Wuhu Shaoda power company revved up its production of electricity, burning a ton and a half of coal per minute to satisfy more than half the demand of Wuhu, an industrial city of two million people. AES Corp., an American energy company, owns 25% of the 250-megawatt facility, which local officials call an "economically advanced enterprise." The Chinese plant is outfitted with devices that prevent soot from billowing into the sky. But other pollutants, such as nitrogen oxides, sulfur dioxide and a gaseous form of mercury, swirl freely from the smokestacks. Rather than install more sophisticated and costly antipollution equipment, the plant, which is majority owned by state-controlled entities, has chosen to pay an annual fee, which it estimates will be about $500,000 this year. That option meets Chinese standards but wouldn't be allowed in the U.S. The airborne output of Chinese power plants like Wuhu Shaoda was once considered the price of China's economic growth, and a mostly local problem. But just as China's industrial might is integrating the country into the global economy, its pollution is also becoming a global concern. Among the biggest worries: the impact of China's vast and growing power industry, mostly fueled by coal, on the buildup of mercury in the world's water and food supply.

Pottinger et al. (2004) in the same online format explained that when massive amounts of mercury have been released into the Earth's atmosphere, deposition into the oceans and on the soils of continents is sure to follow. This might, Pottinger et al. explains, possibly cause contamination of the world's water systems and eventually the food supply. In his report he made specific note of the elemental toxin mercury's extreme detrimental effects on small children and infants stating that the danger of exposure of mercury to the nervous system of fetuses and small children is well documented. Lifelong effects may include mild deficits in memory or attention span or can be as profound as mental retardation. Pottinger et al. further elaborated that the EPA in January of 2004 released research reports that indicated "630,000 babies born in the United States within the 12 month time frame of 1999-2000 had potentially unsafe levels of mercury in their blood. This was, Pottinger et al. stated, about twice as many as the EPA had been previously estimated [*sic*]"

Pegg (2005), reporting for the Environmental News Service on a website, wrote a scathing report on legislation proposed under the Bush administration that addresses the mercury emitted by coal fire power plants in the United States. Pegg (2005) reported on this website that in the United States regulations that govern mercury emissions are being challenged by many states. Pegg explained that the EPA Inspector General had found that regulations had been manipulated to favor the emissions trading plan and stated these regulations were seriously flawed. Senator James Jeffords was quoted explaining, under this rule; hundreds of the oldest, dirtiest power plants won't even control mercury emissions for more than 20 years. That is what this rule gives us, more pollution for longer than the law allows." By manipulating toxic mercury emissions in complex trade regulation this in effect allows the coal plants to forestall clean up efforts and continue to release mercury in the name of free trade and cost controls. All the while more generations of children health are put at risk.

In an online report titled "Cadmium, Mercury, Pesticides: Environmental Chemicals of Concern" (2005) written for the news publication called the Environment News Service, several reports were posted that quoted from the Center for Disease Control (CDC). These reports contained information regarding toxins that might prove harmful to a developing fetus or the mother carrying a fetus and explained the mother could potentially transmit elemental toxins via the placenta. While several elemental toxins were discussed, mercury poisoning and possible medical complications from it were elaborated on within this online site "Cadmium, Mercury, Pesticides: Environmental Chemicals of Concern" (2005) which explained mercury may be passed from the mother to the developing fetus and can cause brain damage, mental retardation,

blindness, the inability to speak and seizures. They stated that children who have been poisoned by mercury can have digestive problems, kidney damage and multiple problems with their nervous systems.

In the same issue of the website, *Environment News Service*, physician Dr. Jane Houlihan was quoted as a spokesperson for the CDC discussing elemental toxins found in the cord blood of new born infants. Dr. Houlihan was quoted in the online report "Cadmium, Mercury, Pesticides: Environmental Chemicals of Concern" (2005) when she explained that exposure to toxic chemicals is of greater concern when the person of interest is a small child, elaborating that when toxic chemicals exposures occur during childhood their effects can be much more harmful than the same dosage to an adult. The dose makes the poison and the size and accelerated growth in a small child makes them the most susceptible to poisoning's effects.

McCaffrey (2004) reported in the online journal *Focus*, for the Harvard Medical, Dental & Public Health Schools, on research that looked for high levels of mercury in children. McCaffrey discussed and expounded upon the causes, symptoms of and treatment of high levels of the elemental toxin mercury currently being measured and diagnosed. McCaffrey (2004) reported in the online journal *Focus* stating that on an 18 year study of 800 children whose mothers had consumed fish and other seafood that contained mercury while they were pregnant showed brain damage to the fetus may be permanent. Some of the long term poisoning effects noted in this study were hearing related signals to the brain, and brain based regulation of the heart rates that were reported to be a result of mercury poisoning within the medulla oblongata these effects were significant well into the teen years. It was further explained that new data suggests

that currently one in six infants may have elevated mercury levels in their blood that exceed what the EPA calls its safe limit. McCaffrey, reported on ground breaking research that examined mercury poisoning which appeared in the *Journal of Pediatrics* explained by discussing mercury's effects on the young child and fetal brain stating," The brain cells don't get a second chance."

Perhaps a common source of mercury as reported by Lorscheider and Summers (1995) in a website review for the *Federation of American Societies for Experimental Biology Journal* (FASEB) is the mercury fillings that in the past were commonly used by dentists. Lorscheider and Summers reviewed a study where mercury levels were measured in patients with mercury amalgam fillings. On this website Lorscheider and Summers (1995) reported that for many years dentists used a silver amalgam containing about 50% mercury. Research has shown that mercury vapors are continually released in the form of vapor in the mouth where it finds its way into the body tissues. Currently research is underway to assess just how much mercury is contributing to the body burden in this manner. With many species of bacteria inhabiting the human gut perhaps mercury follows the same path ways as aquatic systems. More research needs to be conducted on this issue; however, at this time research does not support the continued use of amalgams containing mercury for dentistry as safe.

The New York City Department of Health and Mental Hygiene (2008)[a] has published online warnings to consumers through their website about another possible source of mercury. They discussed herbal and medicinal products from China that they have tested in their laboratories and found to be high in mercury content along with some lead content.

An online website, The New York City Department of Health and Mental Hygiene (2008) [a] reported that within the last few years some herbal remedies imported from China have when analyzed been found to contain high levels of lead or mercury. Two that have shown to have high levels of these toxins are called "Emperor's Tea Pills and Hepatico Extract"

On the same website, with a slightly different link, The New York City Department of Health and Mental Hygiene (2008) [b] reported on medicinal and herbal substances from India with unusual names that indicate their country of origin and have found their way into the United States. After being analyzed in a laboratory, some have been shown to have very high levels of mercury and also lead. These imported products are called "Jambrulin, touted as made for diabetes control of blood sugars, Mahayogaraj Guggulu, a supposed remedy for rheumatic pain, ands Lakshmivilash Ras (Nardiya) as a cough, and cold medicine." This report serves as a warning that in some third world countries, ancient alchemy, not modern medicine, still produces toxic concoctions and these may be imported.

A website for, the Washington State Department of Health (2007) issued a warning about necklaces that have been imported from Mexico that were filled with mercury. The Washington State Department of Health (2007) reported online that some of these had broken at a school causing a hazard to students near by. The shiny quick silver is considered a decorative item in Mexico as this pretty poison is contained in the glass jewelry worn around a teen's neck. The manufacturer in Mexico was apparently unaware of any poisoning threat as imported mercury filled items as jewelry have been manufactured in Mexico and then have come across United States borders.

While mercury poisoning shows many complex symptoms, perhaps some of the most unusual indications of this elemental toxin's poisonous effects on small children were documented by Ellenhorn (1997). This reference text on poisonings described symptoms young children might exhibit when they were suffering from mercury poisoning. Ellenhorn (1997) reported that acrodynia in medical terms means painful extremities. Children suffering from mercury poisoning frequently rub their hands together causing red raw skin and possible secondary infections. In addition teeth are lost as gums ulcerate. Muscle tone becomes very weak and sweating can become profuse as the body attempts to rid itself of the ingested mercury.

The San Francisco Medical Society website issued a warning concerning mercury content in some fish species where Hightower (2001) explained the major concerns of the medical community. Hightower cited the limits established for mercury levels in the blood of children, infants and adults in her essay on this toxin. She further explained with concise descriptions what potentially has occurred to a person's system when they have been poisoned by the elemental toxin mercury.

Hightower (2001) reported online that the FDA and some fish markets have settled in court on precisely how much mercury may be allowed in fish meant for human consumption. In this settlement there were two different categories of fish agreed upon: first, non-predator fish which must have less than 0.5 ppm of mercury in their tissues, and predator fish which were allowed a higher value as mercury moves up the food chain of between 0.5 ppm and 1ppm. The value of over 1ppm was then given the coined term called "the action level" and the court proceedings ordered that it not be sold to the public. Hightower further reported that in 1998 the FDA conducted their last scientific

survey of fish. This study consisted of 25 fish total tested for mercury in the entire United States. Consumer Reports in their February, 2001 issue decided to look into the issue of mercury in fish species. They stated that, of the swordfish they tested, 50% of the time the values for mercury were over 1 ppm. One of the swordfish was shown to be greater than 3 ppm in mercury. Hightower explained that fish tend to accumulate Methyl Mercury in their tissues where it becomes strongly bound and that no amount of cooking in any manner can cook the mercury out of the fish. Methyl Mercury is 100% absorbed by humans when they consume contaminated fish species. The strongest affinity for mercury to bind is found in the human brain and muscles. For the brain of a developing fetus, this can be devastation. The most common method for the human body to rid itself of mercury is excretion through feces and in sweat. Mercury tends to concentrate in the developing fetus as fetuses do not excreted in-utero and do not sweat to rid themselves of this toxin. Hightower elaborates that by the time of parturition the baby's level of mercury can be "30 to 200 percent of that in the mother's blood." Hightower (2001) stated that the biggest polluters of mercury on this planet are the coal-burning power plants and further described problems with complex legislation dealing with this problem.

Hightower (2001) reported online for The San Francisco Medical Society website outlined that what has been called "the no adverse effect level" for mercury at <5.0 mcg/L whole blood. This level is in flux and as Hightower later stated, "Damage from mercury in a fetus's developing brain is permanent." She further describes what is called the "'benchmark dose calculation' (how much you can eat)" applied to mercury contained in fish. The current levels reported by Hightower were "estimated to be 0.1 mcg/Kg body wt/ day. This was to protect fetuses, infants, children, sensitive individuals

from exposure over a life-time. The ‘fudge factor’ is still being debated and can be 3-10 fold.

Hightower (2001) continued in her conclusion on the same website to explain that the chelation therapy common in other types of toxic poisonings is not advised in the case of mercury. She explained that she recommends to her patients that removing the toxin from the diet is best and therefore avoiding mercury in the first place by following the EPA’s guide lines for fish consumption.

In the online article “America's Fish: Fair or Foul?” (2001) from the web based journal *Consumer Reports*, fish and their possible negative effects on consumers who ate certain species were explained. Multiple tests were conducted in laboratory settings on fish purchased from different markets. One of the tests reported was a test for methyl mercury within some species where this research reported the following. “Half of the swordfish samples exceeded the FDA's ‘action level’ for methylmercury[*sic*], which can harm the developing nervous system.”

Mercury can occur in different compounds or in its pure elemental form as a silvery metal according to an online report titled About Mercury and Methyl Mercury (2006). This online center for information is sponsored by the Center for Food, Nutrition and Agricultural Policy by the University of Maryland-College Park. About Mercury and Methylmercury[*sic*] (2006) an online center for information reported that in addition to fish consumption, some mercury salts may be used in skin lightening creams and in antiseptic creams and ointments. Inorganic or metallic mercury particles can be airborne within atmospheric gasses and when they fall to earth they can find their way into soil or sediment at the bottom of water systems. When this inorganic mercury combines with

carbon by bacteriologic action the most common form methyl mercury is the result which quickly moves up the food chain.

Within the same online report, the FDA's limit on the amount of methyl mercury to be safely consumed was noted as being 1 ppm. This online report, About Mercury and Methylmercury[*sic*] (2006) center for information is sponsored by the Center for Food, Nutrition and Agricultural Policy by the University of Maryland-College Park also explained that one of the worst cases of mercury poisoning has been when people consumed bread that had been made from grain treated with a fungicide that contained mercury. They elaborated that in Iraq the fungicide treated grain was made into bread and consumed by thousands. In the United States mercury poisoning occurred when a family in New Mexico ate tainted pork from pigs previously fed with organomercurial compounds. In this case an 8-year old girl in the family lapsed into a coma and a few weeks later her siblings followed with similar clinical signs of severe mercury poisoning. During the time of the mercury poisoning the mother in this farm family was 3 months pregnant and she reported that she consumed the pork from this time until the sixth month of her pregnancy. The new infant was a boy and at the age of 3 to 6 months showed signs of an abnormal electroencephalogram. A full 6 months after the mercury poisoning was detected and all exposures had stopped the infant in the family and younger children showed no improvement from symptoms of mercury poisoning. The dose to size ratio of their body mass indicated their symptoms could be pernicious and long term. The oldest child of 20 years and fully grown at the time of the poisoning showed improved functioning and was somewhat recovered over time as it was assumed mercury was being excreted and levels were dropping as determined by blood testing.

Concern over increasing mercury contamination now and in the future for the general public is expressed in an online document written by, Kay, (2003) who discussed the effects of mercury, its sources and control measures. Kay, (2007) further reported that the concern presently world wide is the tremendous increase in mercury production and different use of this toxic metal resulting in anthropogenic release into the environment. Kay, (2007) further explained that mercury is changed into methyl mercury by organic actions where it readily travels easily up through food chains. All forms of mercury have been shown to be highly toxic to the sum of the biota and are a potent poison to humans especially infants and small children, even in extremely low concentrations.

CHAPTER III

RESEARCH METHODOLOGY

Randomly chosen samples of manufactured products were analyzed in this research. Gay et al. (2006) reported that selecting a sample is a vital step in any research. What was termed the "goodness "of the sample may result in the generalizability of the research conclusions. A good sample he stated is one that truly represents the population from which the research selections have been made.

There are four types of sampling possible within the frame work of research according to Gay et al. (2006), this research utilized a type referred to a cluster research and it best fits the nature of the outline of the problem. Gay et al. explained that cluster research is more convenient when the population is very large or spread out over a large area as is the case within this research. In addition, all members of the group have similar qualities or characteristics. This research was conducted on such items purchased from large chain stores across the United States. The assumption was made that stores of this nature would tend for the most part to have similar items marketed to small children for consumption.

Gay et al. (2006) description of an intact group best fits and applies to this research; it was defined as a population, or a group, of manufactured products for sale to the general public in stores that are part of a nationwide chain. These include but are not

limited to, Wal-Mart®, Kmart®, Dillon's® a subsidiary of the Kroger Company® which maintains a nationwide grocery chain, Target® , Walgreen's®, and The Dollar General Stores®

The steps appropriate for conducting cluster sampling were described in detail by Gay et al. (2006) who explained that there is at least one common misconception in this sampling technique. The correct steps in this type of sampling were listed by Gay et al. (2006) and include identifying the population of interest and then determining the sample size. Gay et al. further elaborated and explained that the researcher must conduct random sampling to be sure all population members are represented within the study

The idea of randomness in a sample is critical as stated by Ott and Longnecker, (2001) who clarified this concept stating that we must understand how a sample is selected to determine probabilities and outcomes of any research. Samples selected in a non-random manner can seriously distort data and selection bias or non-random sampling must be avoided

Ott and Longnecker, (2001) further explains exactly how random number tables are used to reliably choose samples in a random manner by noting that all possible sample sizes are only available when the sample size is very small. Random samples are potentially difficult to obtain however the researcher must try and avoid bias and this could affect any inference made from the research.

Sample size is dependent on the population to be sampled; therefore, some clarity is needed to refine this concept. Gay et al. (2006) elucidated further defining the concept of sample size appropriateness within research. The entire sample is rarely available to the researcher and therefore the accessible population which is available is in reality the

one where sampling can occur. In most research the realistic choices made by the researcher are made not the ideal choices due to constraints within the research.

Selection of Manufactured Products

This research was limited to the accessible population Gay et al. (2006) of samples for sale in stores within four states in the United States where consumable goods may be purchased; those being Kansas, Oklahoma, California and Kentucky. This was due to the geographical location of the researcher during the time when the purchasing of different samples occurred. This was also due to the consideration of travel costs and the costs of the sample items to be tested. In addition, by choosing large national chains as part of the research design as opposed to small local venues, the assumption was made that similar items or the same items are for sale in many or all of the stores in a nationwide chain.

The researcher lives in Kansas and frequently travels to Oklahoma and this common occurrence facilitated purchasing samples in the aforementioned mid-region states. During the sample collection phase of the research, from June 1st, 2007 until January 31st 2009, the researcher traveled to California for a one week visit located on the United States' West Coast and to Kentucky for a one week visit, considered to be in the eastern half of the United States. While Kentucky is not on the extreme east coast, items were purchased while in this location as this researcher deemed this state's location east of the Mississippi river to be considered a geographical indicator of division between east and west within the United States. To better assess manufactured products for sale in the United States, the decision was made to purchase samples found for purchase in

California and Kentucky during these trips, as this was as reported by Ott and Longnecker, (2001) a realistic choice (i.e. accessible), not an idealistic one (i.e. target) is commonly made in research.

In order to reduce bias (Ott and Longnecker, 2001) in purchases, the researcher randomly shopped at multiple stores over the time period prescribed. The researcher made no assumptions about the internal layout of the stores, but walked randomly up and down different aisles and to different areas within the store. If the researcher noticed an item for sale that appeared to fit the criteria, its label was read to determine the country of origin. This has been ascertained by reading the usually small print on the label or tag which commonly states: "product of X" or "made in X".

The criteria set for this research is that any prudent adult would interpret this selected, manufactured item as being meant for oral consumption by or close oral contact with a child six or younger, or potentially including infants. No other descriptors, including the nutritional facts listed on the packaging, were read or noted.

Ott and Longnecker (2001) described the considerations that must be taken into account when choosing the sample size as he stated that an idea called the central limit theorem holds for $n > 30$, with n used to indicate the sample size. This can be interpreted that for most research the sample size should be greater than 30.

Relying on Ott and Longnecker (2001) description, the sample number of 50 total pairs of samples manufactured in the United States and 50 total pairs of samples manufactured outside of the United States were purchased for this research. Ott and Longnecker (2001) stated that *n*, a sample size of >30, was acceptable in many cases if the population is not heavily skewed. The clustered population of manufactured items in

four states is a tremendously large number. In order to reduce bias, the researcher chose to increase the sample size above the *n* indicated of 30, up to 50 pairs, or, 100 total samples from each group. In addition one sample pair consisted of a non edible product and its best fit counterpart of a harmonica manufactured in China and the best fit of a mouth harp made in the United States. This research was on edible items that might vary greatly; for example, gummy worms or animal crackers. These are of course very different and the only commonality between items is that they are both manufactured food items that specifically target consumption by a small child age six and younger. The two groups compared within this research will ask only is there a significant difference in the elemental toxins found utilizing (XRF) technology comparing best fit items manufactured in the United States and those manufactured in countries other than the United States. There will be no assumption made as to the consistency, taste, physical state, "solid, liquid, or colloidal," or any other physical properties of any item. The only parameter focused upon when choosing an item was if these best fit items are edible or made for close oral contact and targeted toward a small child six and under. When a sample fitting the parameters of this research is found, the researcher looked to see if another, identical item is available for purchase. The researcher then checked the price listed and determined whether two identical samples or a pair of samples totals in cost less than $15.00. This will be the artificial maximum limit set by this research due to over all cost involved. If the sample meets all criteria, a purchase will be made. In all cases the receipt for the purchase, indicating where and when the purchase was made, will be kept with the samples.

A rationale for choosing the sample size of 204 total samples, with 51 pairs or 102 total samples of products made in the United States and 51 pairs or 102 total samples of products made in countries other than the United States is also an acceptable sample size as shown by the table published online by the University of Florida on a website where Israel (1992) reported that a minimum of 100 elements is needed for a major group of a large population.

To clarify the above statements, Israel (1992) supplied the following numerical values presented on a table on the same website where population size and sample size can be interpreted as follows:

Table 3

Sample size for ±3%, ±5%, ±7% and ±10% Precision Levels Where Confidence Level is 95% and P=.5

Size of	Sample Size (n) for Precision (e) of:			
Population	±3%	±5%	±7%	±10%
500	A	222	145	83
600	A	240	152	86
700	A	255	158	88
800	A	267	163	89
900	A	277	166	90
1,000	A	286	169	91
2,000	714	333	185	95
3,000	811	353	191	97
4,000	870	364	194	98
5,000	909	370	196	98
6,000	938	375	197	98
7,000	959	378	198	99
8,000	976	381	199	99
9,000	989	383	200	99
10,000	1,000	385	200	99
15,000	1,034	390	201	99

Table 3 (Continued)				
Size of	Sample Size (n) for Precision (e) of:			
20,000	1,053	392	204	100
25,000	1,064	394	204	100
50,000	1,087	397	204	100
100,000	1,099	398	204	100
>100,000	1,111	400	204	100
A = Assumption of normal population is poor (Yamane, 1967). The entire population should be sampled.				

Source: Israel (1992)

It should be noted that in the last column where the population is > 100,000, a sampling size of 100 is given under the column $\pm$ 10%. While this is a fairly large percent, the time and financial constraints leave this research unable to move to even the next category of $\pm$ 7 % where 240 paired samples would have to be purchased to conduct this research. It is assumed that the population of this research is above or >100,000 as it includes all manufactured items for sale in the United States, meant for oral consumption or close oral contact by a child six or younger including infants.

Research Instruments

The technology currently exists to analyze samples within seconds using a non-destructive method. This technology is called an X-Ray Fluorescent Spectrometer (XRF). As explained by "Environmental Analysis by XRF" (2008), this device was used to analyze samples for three elemental toxins: lead, bromide and mercury. This investigation involves the analysis of manufactured products that specifically target small

children and infants. All manufactured products will be sub divided into two groups: products made in the United States, and those made in other countries. Within this investigation both groups of products will be analyzed with an X-Ray Fluorescent Spectrometer (XRF) and the results compared. The XRF located in the Physical Sciences building at Oklahoma State University will be the major instrument for analysis. A focus will be on the three well-documented elemental toxins, lead, bromide and mercury. However if other elemental toxins are analyzed in any sample occurring at levels high enough to be significant as determined by acknowledged experts such as Ellenhorn, (1997) their presence will also be noted. Set and identified levels of elemental toxins of concern will be reported before measurements occur.

An X-Ray Fluorescent Spectrometer (XRF) is a non-destructive tool for analysis that can measure individual elements in tiny increments, those being parts per million, (ppm) or parts per billion (ppb). This study will use an XRF as explained by "Environmental Analysis by XRF" (2008).

An X-Ray Fluorescent Spectrometer (XRF) has become a useful tool at the Mount Sinai Medical center in New York to test for the accumulated lead in a person's bones as reported by the online site, "Measuring Lead in Bone; the Physics of Bone Lead X-Ray Fluorescence" (1997). This website is sponsored by the Mount Sinai Medical Center in New York City through the Department of Community and Preventive Medicine within that medical center who stated that many elemental toxins or heavy metals can be measured with standard lab analysis stating that the principle of X-Ray Fluorescence (XRF) is to use photons of light in the X-Ray spectrum to be absorbed by a sample. When this occurs the electrons at the lower levels of each atom within a sample are in

essence thrown out of the orbital or ejected. The Aufbau principle of electron energy states that all electrons will occupy the lowest energy level orbital when available. With a newly empty energy level now available, the other surrounding electrons that have been in higher levels cascade downward to fill in, forming what is referred to as bremsstrahlung radiation. "Measuring Lead in Bone; the Physics of Bone Lead X-Ray Fluorescence" (1997) explains that this cascade effect then releases a subsequent energy pattern that is unique to each element and can be determined by computer analysis. The presence of heavy or toxic metals can be measured within a person's body in the non evasive way.

Figure 1. Words Into Action. Andrew Todd Monitors the Spectrum as an Assistant Positions the XRF Machine to Measure Tibial Bone Lead in a Subject.

Source: http://www.ehponline.org/docs/1995/103-7-8/NIEHSnews.html

The Mount Sinai Medical Center in New York City is on the leading edge of research in preventing lead poisoning by using XRF technology. This precision machine

is also used widely in research to analyze samples from ancient artifacts. This non-invasive device has proven to an invaluable research tool, as elucidated in the on-line Journal *Science Daily* in an article titled, "X-ray Technology sheds light on ancient stone inscriptions" (2005) which reported that faded text on ancient stones could be analyzed using (XRF) technologies. This precise tool has already gained prominence world wide on multiple scientific circles as within multiple disciplines very accurate and consistent measurements can be made.

As researchers world-wide have become aware of the XRF's non-destructive capability in maintaining the integrity of the sample being analyzed, it has been utilized in ever broadening fields. In addition to the almost instantaneous results displaying the elemental make up of the sample, the use of this device has become a standard for analysis. The history of the XRF and explanations of the physics of its internal workings was described online in a report by Guthrie (2008) as follows:

> 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 counting the number of photons of each energy emitted from a sample, the elements present may be identified and quantified.
>
> Henry Moseley was perhaps the father of this technique, since he, building on W.C. Röentgen's discovery of the high-energy radiation dubbed X-rays, built an X-ray tube which he used to bombard samples with high-energy electrons. Moseley in 1912 discovered a mathematical relationship between the element's emitted X-ray frequency and its atomic number. In 1925 Coster and Nishina were the first to use primary X-rays instead of electrons to excite a sample. After Glocker and Schreiber were the first to perform quantitative analysis of materials using XRF in 1928, detector technology had to catch up in order to make the technique practical, which didn't begin to happen until the 1940's. The 1950's saw the first commercially produced X-ray spectrometers. In 1970, the lithium drifted silicon detector was developed, and this technology is still in use today. 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.

Within a recently published dissertation, assessing exposure to polybrominated diphenyl ethers (PBDEs) in the home environment: Linking sources to personal exposure, Gardner, (2008) explained that an (XRF) was utilized to determine the ambient level of bromine in products. The possible source of the bromine within this study, Gardner (2008) is Polybrominated diphenyl ethers (PBDEs) a type of fire retardant compounds in common use on many house hold items. Gardner (2008) stated that the use of an (XRF) to precisely measure the bromine found in manufactured consumer products was invaluable. Gardner (2008) also discussed the problem of the matrix effect explaining that this could cause potentially faulty readings in some samples. To compensate for this Gardner explained some samples were embedded in glass to create a sample with a smooth surface before it was analyzed.

One of the problems with the (XRF) was an interference caused by the uneven surface of a sample, called the physical matrix effect. In addition the chemical matrix effect can confound data due to the difference in the concentrations of interfering elements within the sample being analyzed.

To compensate for this effect, samples in other studies have been embedded in glass to create a sample with a smooth surface before evaluation. The matrix effect could potentially have caused a faulty reading in some samples due to dispersement of X-rays from uneven surface structures. However a newer technology where a low angle of incidence is used lessens this problem as explained by Guthrie (2008) in the same on line analysis that reported that the matrix effect was eliminated if the sample was reduced to

thin film analysis. This he explained was achieved by directing the X-ray source at very low angles of incidence toward thin film samples.

The hand held Niton® XRF, manufactured by Thermo Fisher Scientific, utilizes newer technology as the device is held directly on the sample making physical contact. There is a safety device on the front end of the Niton® (XRF) that will not allow X-rays to be emitted unless there is physical contact made. This reduction of angle and physical contact largely negates scattering due to uneven surface structures and therefore helps to eliminate the matrix effect. The Thermo Fisher Scientific®, Inc. company which manufactures the hand held Niton® XRF posted the following description along with a photograph of their devises Niton® analyzer products (2007) and describes this instrument as delivering lab-quality results with great precision and accuracy.

Figure 2. Niton Analyzer Products.

Source: Retrieved July 16, 2008, from Thermo Fisher Scientific, Inc. Website: http://www.niton.com/NITON-Analyzers-Products/default.aspx

The Thermo scientific company has graciously agreed to loan one of their hand held Niton® XRF's for use in this research. This will enable this research to double check all initial analysis with a second highly reliable and independent machine. Any sample indicating significant levels of lead, bromine or mercury in reported data in the results from the X-Ray Fluorescent Spectrometer at Oklahoma State University will be reanalyzed using the hand held Niton® XRF. Additionally the safety latch prohibits some objects being analyzed within the large XRF such as the harmonica, therefore it will be analyzed with the hand held Niton® XRF.

The researcher will first place all samples into the large (XRF) located at Oklahoma State University and then conduct analyses for sixty minutes read time per each sample.

Multiple standard samples will be precisely prepared and analyzed for a full sixty minutes containing each toxin of interest. The values established for lead content will aligned with published government standards of .1ppm, while bromine content will be set at 125 ppm and mercury of 1 ppm. The Limits of Detection in Spectroscopy, (2003) explain that the International Union of Pure and Applied Chemistry (IUPAC) defines the limit of detection as the concentration or the quantity derived from the smallest measure, that can be detected with reasonable certainty. IUPAC further suggested in this publication that because the values for these blanks are estimates based on limited measurements a 3 standard deviation value corresponds to a 90% confidence level. Given this definition in relation to this survey where .05 alpha has been established a confidence level of 95% was desired and therefore 5 standard deviations above the mean was calculated. The total of 102 samples was conducted for 120 minutes each with 50% dead

time or a full hour of analysis each. The region above the concentration at which we can decide whether lead or bromine is present or not, will establish the limit of detection for this survey with a comparison of precision of the instrument and concentrations graphically represented, refer to **Figure 3**.

Research Design

The design is the general plan that is undertaken that includes the basic outline and goals of the research. Gay et al. (2006) described the research design stating that a description of the basic design of a study should indicate the basic structure and goals of a study. The design of any research may fall into different categories. This study was a type of design classified as descriptive research, specifically comparative survey research.

Gay et al. (2006) further elaborated on this design explaining different sub groups within research designs. He describes "Types of Surveys" and clarified that this type of research can be classified in more than one way. Descriptive research is used to gather information concerning the current status of the particular phenomena or to describe what is real with respect to variables in a situation. Gay et al. (2006) further elaborates that for a survey study to be justified the researcher must set specific objectives that indicate the exact nature of the information that is desired to be obtained. Typically it is noted that survey type research has inherent problems with nonresponse. The nature of this study is to analyze randomly purchased samples for elemental contaminates, therefore this concern was not applicable. Descriptive research utilizing survey methods then reports on and describes the way things are. This study will report the levels of elemental

contaminates that are found to be present and in what concentrations, specifically lead, bromine and mercury in order to identify samples where future research might focus.

Within this research we, through random purchase of manufactured items in multiple national chain stores, control for external validity. These purchases were within three regions within the United States to attempt to even better control external validity. External validity, Ott and Longnecker (2001) is the ability of the research to generalize the results found within the research to the entire population. The entire population of this survey will be all manufactured items that target children six and under that are edible or come into close oral contact that can be purchased in the United States. This population would be a tremendous number and as previously covered a sample of two hundred and four total that consist of fifty one pairs of items manufactured in the United States and fifty one pairs of items manufactured in countries other than the United States will be utilized due to cost and time constraints. Ott and Longnecker (2006) described threats to external validity stating that threats affecting the group to which results will be generalized and threats that affect generalizations to what or the settings, conditions and variables to which results can be generalized (p. 241).

Internal validity is considered to be critical to a studies design. While controlling threats to both external and internal validity are both important, there is a catch 22 phrase that is used to describe the complications of these ideals. Gay et al. (2006) describes internal and external validity paradox stating that all research must strive for balance between the two ideals of control and realistic ideals. If any choice is involved within research one should err on the side of control as a study without internal validity is worthless.

In this survey type study we will instigate rigid controls as samples are handled and analyzed using the XRF machine. Gloved hands and precise lab specifications for handling samples will be utilized. Samples will be loaded into CertiPrep #3529 31mm X-Cell, XRF liquid cells and sealed with polyester spectro-film ultra thin mylar (.00014") from the Somar International Inc. # 3615-33 pre cut 76 x76 mm. In order to lessen the matrix effect comparisons of values deemed significant as read by the XRF were finely ground using an onyx mortar and pestle to achieve uniformity in surface texture. Every attempt will be made to insure all samples are not contaminated in any manner throughout all processes involved within the (XRF) analysis.

The third component of survey type design is that it must have a control. This research will use a type of design called the Posttest-Only Control Group design. This specific type of research is described in an on line website, Research Methods, Knowledge Based by Trochim (2006) which explained that we are interested in the determination only if these two groups being surveyed are different.

Mortality refers to the reduction in the number of participants called attrition, Ott and Longnecker (2001). This survey will analyze samples purchased at stores and therefore attrition or mortality will not be a factor.

The control in this research was the randomly chosen member of the pair of samples to be tested. Each pair in random order was made ready to be analyzed in the (XRF). To facilitate this they were handled with the following prescribed format.

1. They were purchased randomly in well known national chain stores where products for children are available to the consuming public.
2. They were kept in their original containers.

3. The pair of identical samples was then sealed in zip lock bags separately.
4. The pairs labeled as made in the United States were labeled on the zip lock bag sequentially US1A, US1B, US2A, US2B etc. (United States). The pairs of samples made in countries other than the United States was sealed in the same way and labeled on the zip lock bag with OC1A, OC1B, OC2A, OC2B etc. (Other Countries). Pairs were labeled in random order that the number matches the best fit of samples to be tested.
5. When the analyzing process was about to start the researcher randomly flipped a coin for each pair. If the coin side of heads is up, then sample A was analyzed; however if the tails side of the coin was up, sample B was analyzed. The remaining sample was not opened or adulterated in any way but remained as a control in this research.
6. After the randomly chosen sample is analyzed its ROI count will be used in statistical programs to determine if there is any difference between groups.
7. All samples were kept sealed in their individual zip lock bags and will be available for inspection. Only a few sub samples will be used from each full size sample and the (XRF) technology is of a non destructive nature therefore samples will be unadulterated in any way. For example, from a box of cookies perhaps three cookies total or less will be analyzed from the entire large box purchased of cookies. A random selection by blindly reaching into each container will be made to obtain specific items to be analyzed.

8. The following hypotheses were made in this comparative survey study.

H_0 There is no significant level of any elemental toxin detected in any sample tested from sample groups of products.

H_{01} There is no significant level of elemental toxins detected in products that were manufactured in the United States but significant levels of elemental toxins will be detected in products manufactured in countries other than the United States.

H_{02} There is no significant level of elemental toxins detected in products manufactured in countries other than the United States, but significant levels of elemental toxins will be detected in products manufactured in the United States.

H_{03} There is no significant level of mercury found in any sample tested, but other elemental toxins will be detected at significant levels, specifically, lead and bromine.

Pilot Introduction to XRF Usage and Training

In the summer of 2007, Dr. Allen Apblett explained the usage of an X-Ray Fluorescence Spectrograph to this researcher. We were shown the device located on the third floor of the Physical Science building at Oklahoma State University, and demonstrated its usage by placing a ring in the machine to analyze the metals it contained. It was explained that a dosimeter must be worn at all time when using the XRF as per Oklahoma State University rules. Through manipulation of computer controls there was produced a print out that showed a graphic display with several peaks shown. Among these were Au (gold), Ag (silver) and Cu (copper). The print out was displayed graphically and showed the amount of each element that was contained within the sample

in the ROI counts indicated. This was the first time this researcher had been introduced to the XRF technology.

A discussion occurred with this researcher including different items that could be tested in the XRF and possible problems such as the matrix effect. During December of 2007, this researcher received a communication referring her to a website that explained the history and internal workings of an X-Ray Fluorescent Spectrograph. This researcher was instructed to study this information as it would be required on the upcoming qualifying exams for doctoral candidacy. Special emphasis was placed on resolving the issue of the matrix effect.

This researcher studied the information provided and was notified in the spring of 2008 that she passed all of her qualifying exams which included a question that covered the internal workings of the XRF and the associated matrix effect.

During the spring of 2008, this researcher discovered a website for the Thermo Fisher Scientific Company. The website announced a free seminar which this researcher attended. The seminar was very educational with a Power Point presentation and question and answer session covering the internal workings and usage of an XRF.

This researcher was privileged to hold and be instructed in the use of a Niton XRF during this seminar. During the same seminar, this researcher was informed that the Thermo Fisher Scientific Company supports educational endeavors and a loan of their equipment was a very realistic option. This researcher was assured that the Thermo Fisher Scientific Company representative would be able to loan a hand held Niton XRFs for this researcher to utilize to complete this research. This additional safeguard within this research will enable this researcher to overcome some of the possibility of error as

two separate machines will be used in all reported results that are of a significant level for elemental toxins.

In the summer of 2008, this researcher studied the material required for approval to use the X-Ray Fluorescence Spectrograph at Oklahoma State University. The appropriate tests were taken to ensure university standards for radiation safety. This researcher completed this task and was issued a dosimeter along with appropriate certifications.

The actual analysis of samples took place in the fall months of 2008 from early October and continued through January of 2009.

Data Collection Plan and Recording

A spread sheet with pre-labeled grids will be used to record all data. The researcher will print all data saved on the computer in the lab room on campus at Oklahoma State University, where the XRF is located. An abbreviated sample follows:

Table 4

Table of Elemental Toxins in Counts in Area of Interest Indicated After Analysis of Samples

	Pb	Br	Hg	Other
US1 Animal shaped cookies				
OC1 Animal shaped cookies				
US2 Marshmallows				
OC2 Marshmallows				

Data will be entered in into the spread sheets as is shown with significant levels for each elemental toxin as established by United States government agencies. A complete spreadsheet of samples purchased for this study is located in appendix of this manuscript. All readings completed by the (XRF) located at Oklahoma State University are saved on the computer located in the same room. A print out of the graphical display can be made of any readings. A print out in the area of interest for bromine and lead and mercury will be created for each sample if these toxins in ROI units are determined to be present. Some printouts deemed applicable for this survey are located in appendix B of this manuscript.

A description of the (XRF) internal workings when the lid is opened includes a rotating tray where at most ten unknown samples can be placed and a time length of analysis set for each before the analysis occurs. The time frame to ensure accuracy will be a full two hour or one hundred and twenty minutes running for each sample. The XRF reads the sample and then saves the reading, alternatively, each of these functions occurring over this specified time frame. Therefore one half of the time frame or one full hour will be reading and one half recording. In addition multiple blank samples were run to set a standard for the computer to read as it relates to the samples being measured.

Multiple very exact standards were made from standardized lead solution; this standard solution was made and introduced into the (XRF) to set a known value to determine concentrations for the computer to interoperate as it sets the limits of detection for all samples to be analyzed for lead. In addition multiple exact standards for bromine were made from known bromine solutions to determine concentrations for this toxin.

Pb	Lead in candy likely to be consumed frequently by small children: Recommended maximum level and enforcement policy, FDA, (2006) is recommending that lead levels in candy products likely to be consumed frequently by small children not exceed 0.1 ppm because such levels are achievable under good manufacturing practices and would not pose a significant risk to small children for adverse effects. This recommended maximum level of 0.1 ppm for lead in candy likely to be consumed frequently by small children is consistent with the FDA's longstanding goal of reducing lead levels in the food supply to reduce consumers' lead exposure to the lowest level that can be practicably obtained.
Br	What the Pesticide Residues are on Food: EPA (2008) reported that the "Residues of inorganic bromides (calculated as Br) in milled fractions derived from cereal grain from all fumigation sources, including fumigation of grain mill machinery, shall not exceed 125 parts per million" US EPA Pesticides and Food: What the Pesticide Residue Limits are[sic] on Food.
Hg	Hightower (2001) The "benchmark dose calculation" (how much you can eat), was estimated to be 0.1 mcg/Kg body wt/ day. This is to protect fetuses, infants, children, sensitive individuals and exposure over a life-time. The "fudge factor" is still being debated and can be 3-10 fold, depending on which report you read.…Over 1.0 ppm**.** was the FDA "action level," and was not to be sold on the market.

Other Many other elemental toxins might be found when samples are analyzed. These include but are not limited to the following known elemental toxins:

1. Cadmium
2. Chromium
3. Arsenic

If any other elemental toxins are found at significant levels within any sample analyzed, it will be compared to toxins researched using Ellenhorn (1996) or other United States government agencies as an authority. Many agencies overlap and, therefore, the most appropriate source for each published toxin will be cited due to continually shifting and updating findings based on the most recent research. Such elemental toxins will be indicated with their symbol from the periodic table that will be used to fill in the spread sheet along with the (ppm) of that element detected in the sample.

A precise spread sheet of all sampled items will also be created that gives exacting and appropriate information on each sample. **Table 5** is an example of proposed spread sheets inclusive of actual sample items.

While sample items are described as best fit, meaning every reasonable effort will be taken to find a manufactured item that matches as closely as possible and could be substituted for the sample in question, this researcher had considerable difficulty finding some best fit items made in the United States. A specific example of this dilemma was to best fit to a metal harmonica found for sale in multiple stores. A harmonica was found in the children's toy section and was specifically targeted toward small children and made to be taken into the mouth of the child for extended amounts of time as they play the instrument. While this researcher undertook an exhaustive search for a harmonica made

in the United States, none was found to exist for purchase as new. This researcher was advised to substitute another metal instrument specifically made to be held in the mouth and that a child could reasonably play and an instrument called a mouth harp was found that was manufactured in the United States. This was approved as a substitute for best fit in this case as considered to be as close as possible a finding after an exhaustive search, a sample as similar as is possible will be substituted. A complete table of items is available in Appendix A of this manuscript.

Table 5

Example of Table of Samples to be Analyzed for Elemental Toxins

Item	Size	Made In	Description	Retailer & Cost
US1 Animal shaped cookies chosen by coin flip- A *	10 oz.	U.S.A.	Red and blue box with animal cookie pictures on front	Target® Kansas $1.99 each
OC1 Animal shaped cookies chosen by coin flip – B *	1 lb. 1.64 oz (500g)	Mexico	Red and Yellow bag with clown cartoon	Dollar General® store Oklahoma $1.00 each
US2 Gummy multi vitamins Chosen by coin flip – B *	70 gummy vitamins	USA	Plastic bottle with cartoon on label	Wal-Mart ® Kansas $5.49 each
OC2 gummies vitamins Chosen by coin flip –B *	60 gummy vitamins	Germany	Plastic bottle with cartoon on label	Wal-Mart® Kansas $6.36 each

* Coin flip is an example as actual testing has not occurred at this time.

Analysis of Data

Data were gathered using a computer that saved all counts of interest at the time of each analysis. If significant levels of elemental toxins are found, then these samples will be analyzed a second time and the two resulting measurements averaged. Periodically, Dr. Apblett monitored the research to verify that all procedures are being followed appropriately. The use of a hand held Niton XRF will be employed in a second trial. All values were recorded and saved on the computer located within the same room as the (XRF) whose values are derived from the XRF located at Oklahoma State University.

Data were introduced into a statistics program and one-way ANOVAs conducted to determine if the two groups being compared are different. These statistical tests will show variability between the two established groups in lead, bromide and mercury content. A one-way ANOVA is described by Gay et al. (2006) as a simple or a one-way test that is a type of parametric test. The idea behind an ANOVA is that the variation between groups and the variation within groups can form a ratio in this test. This ratio is called the F ratio. The differences between groups become the numerator and the variation between groups becomes the denominator. The greater the difference in an F value, the larger the difference is determined to be between the two groups to be analyzed. Once the F value is calculated to determine if it is significant, this value is compared to an F table where the appropriate degrees of freedom are set for this specific research. The degrees of freedom are a combination of the following ideals; the number of groups and the number of participants involved within the particular research.

Within the data analysis, a comparison will be run with a one way ANOVA on the three elemental toxins of interest in this research: lead, bromine, and mercury. The two groups compared will be the sample products labeled as made in the United States and the sample products labeled as made in other countries than the United States. An alpha level of 0.5 will be established for each of the ANOVAs.

Results will be calculated and shown graphically and with F values posted for each given to interoperate the resultant data. In this manner F values will be discussed and graphical representations made of any toxins found to be present at a significant level.

CHAPTER IV

ANALYSIS OF DATA

This study utilized XRF, X ray Fluorescence technology, to analyze for elemental toxins in samples. The data were supplied by the large XRF machine located in the physical science building of Oklahoma State University and is given as a unit called "Region of Interest" (ROI). Any given sample analyzed is stored in the memory of the computer attached to the XRF and located within the same room.

To analyze the data from any sample, we named the sample and that name was entered into the computer as each sample was individually placed into the center area of the machine. The center region of the machine rotates once for each set time parameter established. Samples for this study were named as previously described being, US1, US2, US3, referring to the sample being manufactured in the United States and numbered randomly after a coin toss. Additionally best fit samples were named OC1, OC2, OC3, referring to the sample being manufactured in a country other than the United States. All samples were matched as well as were reasonably possible. The controls on the XRF were set to run an analysis for one hundred and twenty minutes or two full hour for each sample with one half of the time frame reading the sample and one half of the time frame recording the reading. A reading could be attained by the XRF after only a few seconds of time however by setting the XRF to read the same sample for a full hour great care as taken. This extended time frame was in essence an avenue to facilitate many trials over

the three thousand six hundred seconds in an hour for each sample which are all combined and analyzed by the computer to confirm elemental toxins. The time frame of two full hours was set as there is a 50% dead time while the XRF reads the sample then records data alternating each function.

The sample is analyzed as previously explained by bombarding it with high energy X rays causing lower level electron to be ejected and then the upper level electrons to cascade downward to fill in each empty orbital surrounding an atom.

Each element has a unique configuration of electrons and, as the upper electrons cascade downward, they gave off specific frequencies of light waves which are collected and interpreted by the computer in the XRF. Each specific set of frequencies then registers and reports which elements have been detected. At any time period after all samples are analyzed, the researcher may access the stored information for each.

The saved information must be individually formatted for each sample run. This is achieved with multiple steps using the computer applications of the XRF. Initially, when the results appear on the screen, the peaks are non distinct and not labeled with the chemical symbols of elements. For each sample the cursor was moved to a small icon like a finger print and clicked on it. This icon tells the computer program to identify the peaks found in the sample. The screen previously without element symbols now displays them. A specific example of this would be Br would now appear above a peak where before there was no symbol displayed.

Each element has a specific range referred as the ROI or region of interest and we moved the cursor to highlight the range of this region for the element in question. The region of interest for Bromine was determined to be 11.66 keV through 12.16 keV and

the range for lead was determined to be 10.38 keV through 10.72 keV. These values are established and printed on special periodic tables that are utilized for XRF analysis. A volt is a unit of force or electrical pressure, used to measure the movement or change of a charge from one position to another. A keV is the abbreviation for kiloelectron volt and represents one thousand electron volts given in notation (10^3 eV).

The range determined for Bromine is the total area between 11.66 keV and 12.16 keV as read by the XRF. This area was highlighted and color coded, to tell the computer the specific region of interest to record the number of counts of frequencies detected in a sample. As a clear picture of this peak is desired another icon is chosen to enhance this particular area. The enhancement icon was pressed a total of three times for each sample obtained for consistency. As this process was undertaken the area of interest is centered on the screen and enlarged to show detail.

This process was repeated one hundred and two times over a time period of several months as samples were analyzed for this study. Some printouts of samples are available for this survey in Appendix B. In the upper right hand corner of the print out under the name of the sample is the ROI count. This numerical value is representative of the total counts within the area chosen and therefore the total amount detected of the suspect element.

Great caution must be taken before assumptions are made utilizing XRF technology as the matrix effect, or scattering of light waves from uneven surfaces can cause faulty readings to occur. Additionally the matrix effect also refers to the chemical matrix effects which result from the difference in the concentrations of interfering elements. The initial readings were taken and compared to the mean of standardized

controls. Tables were prepared of the ROI counts for all samples US and OC inclusive of 1-50 for this analysis. These are side by side to facilitate a comparison. A column was included with the difference between the samples manufactured in the United States and those manufactured in countries other than the United States. The samples that were calculated as significant or above **16424 for lead are bolded and an asterisk added**. The samples that showed higher ROI counts above the standardized controls means plus 5 standard deviations or above **377472 for bromine are bolded and an asterisk added.** These tests were utilized to examine the hypotheses explained fully after Table 6.

Table 6

Samples ROI counts US1-US50 & OC1-OC50

ROI counts of Samples 1-25	**ROI counts 10.38keV-10.72keV Pb**	**Difference ROI (Region of Interest) count for best fit pairs**	**ROI counts 11.66keV-12.16keV Br**	**Difference ROI (Region of Interest) count for best fit pairs**
US1	15420		36383	
OC1	**17321***	> 1901	39429	>3046
US2	14618	>579	26155	>1678
OC2	14039		24477	
US3	14204	>3545	36554	>7879
OC3	10659		28675	
US4	13316		25969	
OC4	13416	>100	26721	>752
US5	10872		26886	
OC5	15962	>5090	46852	>19966
US6	14971		25331	
OC6	15202	>231	26021	>690
US7	12604		22738	
OC7	13714	>1110	24013	>1275
US8	13107	>36	22651	>1357
OC8	13071		21294	

Table 6 (Continued)

ROI counts of Samples 1-25	ROI counts 10.38keV-10.72keV Pb	Difference ROI (Region of Interest) count for best fit pairs	ROI counts 11.66keV-12.16keV Br	Difference ROI (Region of Interest) count for best fit pairs
US9	13307		24194	
OC9	14986	>1679	26656	>2462
US10	13440		23410	
OC10	14680	>1240	26420	>3010
US11	6325	>2002	21708	>11758
OC11	4323		9950	
US12	9310		25735	
OC12	**18712***	>9402	35134	>9399
US13	13239		34450	
OC13	**19186***	>6000	38289	>3839
US14	15288	>2172	41071	>1193
OC14	13116		39878	
US15	14864	>1261	51793	
OC15	13603		67909	>16116
US16	12768		22619	
OC16	14021	>1253	26011	>3392
US17	15103		121815	>65212
OC17	**19234***	>4131	56603	
US18	7831		18916	
OC18	**17524***	>9693	87935	>69019
US19	8038	>1869	18257	>2430
OC19	6169		15827	
US20	6289		14414	
OC20	6336	>47	22817	>8403
US21	14217		36242	>1938
OC21	14754	>537	34304	
US22	9571		16867	
OC22	13617	>4046	24461	>7594
US23	14145	>534	24402	
OC23	13611		25672	>1270
US24	14338		29449	
OC24	16614	>2276	49706	>20257
US25	15157		29254	
OC25	16443	>1286	36923	>7669

Table 6 (Continued)

ROI counts for samples 26-50	**ROI counts 10.38keV-10.72keV Pb**	**Difference ROI (Region of Interest) count for best fit pairs**	**ROI counts 11.66keV-12.16keV Br**	**Difference ROI (Region of Interest) count for best fit pairs**
US26	9083	>2497	34060	>19308
OC26	6586		14752	
US27	14656		26061	
OC27	15845	>1189	27183	>1122
US28	14244		26682	>546
OC28	14761	>517	26136	>806
US29	14117		25330	
OC29	14931	>814	25880	>550
US30	13118		23341	
OC30	13400	>282	23929	>588
US31	14966	>1231	48875	>14313
OC31	13735		34562	
US32	13425		23696	
OC32	15114	>1689	26218	>2522
US33	14520	>2280	24996	>784
OC33	12240		24212	
US34	13337		29044	>1364
OC34	15832	>2495	27680	
US35	15726	>702	44860	
OC35	15024		207767	>162907
US36	14536		22274	
OC36	14776	>240	26312	>4038
US37	14315		39420	>11827
OC37	15250	>935	27593	
US38	14267		24292	
OC38	15562	>1295	26854	>2562
US39	14504		38751	
OC39	14681	>177	100548	>61797
US40	11830		21662	
OC40	13438	>1608	23666	>2004
US41	13848	>263	29284	>3794
OC41	13585		25490	
US42	8737		14053	>18593
OC42	13461	>4724	32646	
US43	13619		25361	
OC43	14571	>952	25989	>628
US44	13962		24590	
OC44	**17182***	>3220	32547	>7957

Table 6 (Continued)

ROI counts for samples 26-50	ROI counts 10.38keV-10.72keV Pb	Difference ROI (Region of Interest) count	ROI counts 11.66keV-12.16keV Br	Difference ROI (Region of Interest) Count
US45	**17176***	>1926	29392	>2550
OC45	15250		26842	
US46	14185	>1203	25386	
OC46	12982		25878	>492
US47	10509		41007	>17580
OC47	12049	>1540	23427	
US48	15041	>1656	36013	>6010
OC48	13385		30003	
US49	14994	>1154	34731	>8848
OC49	13840		25883	
US50	14553	>3767	191370	
OC50	13840		363191	>171821

Values both bolded * are significant for lead or bromine content

The samples that were analyzed by XRF in this survey type research that had values above **16424** ROI counts and were then considered significant for lead content are a preliminary finding in this study. Samples were taken in the form they occur and analyzed to attain a rough idea from the one hundred and two sample total within this study. Some of the samples above have been identified as statistically significant as above the value of **16424** are only in fact a few digits above this cut off point. Samples above **16424** were finely ground with an onyx mortar and pestle to achieve uniformity as near as was possible to a uniform structure, results were similar or identical to initial trials.

A calibration curve (Figure 3) was constructed using 2.70, 5.45, and 9.91 ppm standards produced by diluting a NIST-traceable 1000 ppm. A linear relationship was obtained from which the concentration of lead could be calculated using the number of counts from the lead region of interest in the XRF spectrum:

[Lead] (in ppm) = = 0.001345(Counts) - 20.591837

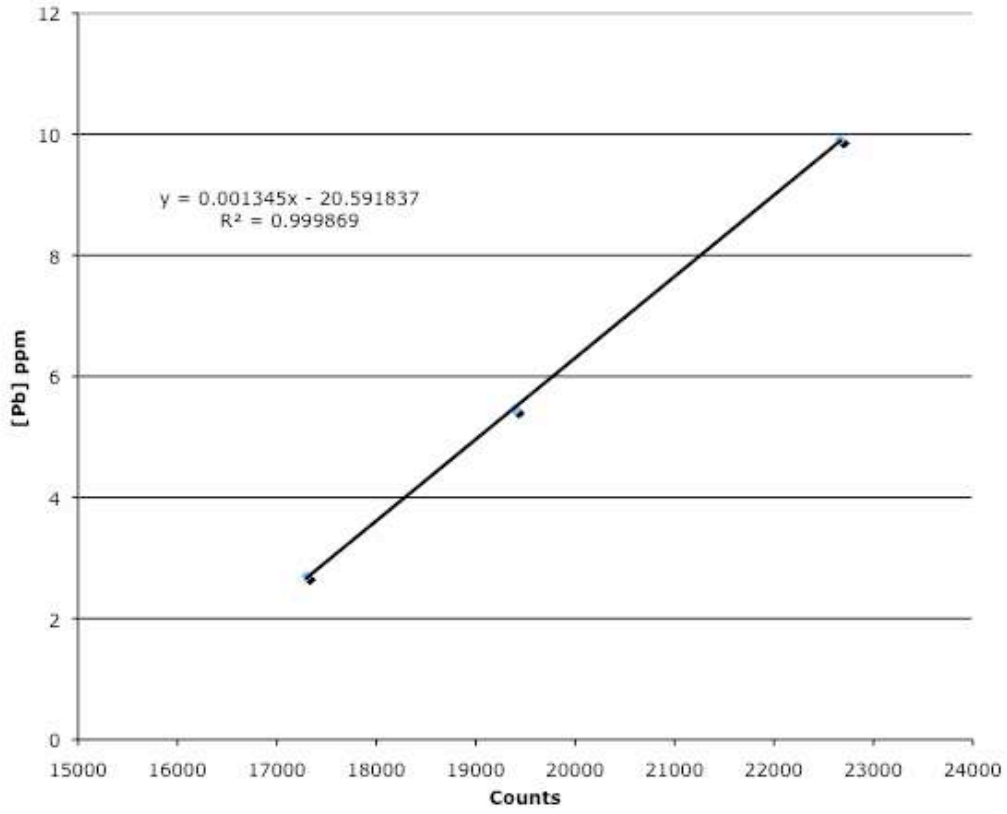

Figure 3. Lead Calibration

In order to determine the limit of detection for lead, glucose was used as a sample blank since it can be considered to be representative for the foodstuffs that were investigated. The average background count for five samples was 13648 counts and the standard deviation (s.d.) was found to be 555. Using a value of 5s.d. as a basis for detection of a peak above the background, any sample with counts above 16424 would be considered positive for lead content. This corresponds to a detection limit of 1.49 ppm.

There were 9 total samples that showed higher ROI counts above 16424 for standards run for lead content of these 8 were from other countries and then imported and one was labeled as made in the United States.

Among multiple initial null hypotheses the following decisions were made;

1. H_0 There is no significant level of any elemental toxin detected in any sample tested from ether group. We reject H_0 as there were significant levels of elemental toxins found within both groups.

2. H_{01} There is no significant level of elemental toxins detected in products that were manufactured in the United States, but significant levels of elemental toxins were detected in products manufactured in countries other than the United States. With the analysis of data gathered we conclude that we reject this null hypothesis. Of the combined analysis of ROI counts of lead and bromine that are statistically significant, being 9 total samples of edible products, 8 of these were manufactured in countries other than the United States and only one is manufactured in the United States.

3. Additionally null hypothesis H_{02} There is no significant level of elemental toxins detected in products manufactured in countries other than the United States, but significant levels of elemental toxins will be detected in products manufactured in the United States. We reject this hypothesis as there were significant levels of elemental toxins detected in products manufactured in countries other than the Unites States.

There were four standards created for lead content from lead standardized solution whose print out may be found in appendix A. The four standards ROI were 13783, 12946, 14583, and 13892. Only these few samples above notated showed ROI counts above this level deemed significant of **16424 for lead**. It must be clearly stated that a blank sample was also analyzed containing only distilled water and this yielded an ROI count of 14843 accounting totally of background scatter. Likewise solutions were created of known bromine content and analyzed as standards for comparison in this survey of elemental toxins.

A calibration curve (Figure 1) was constructed using 9.09, 19.5, 49.5, 98.5 and 985 ppm standards produced by diluting a NIST-traceable 985 ppm standard solution. A linear relationship was obtained from which the concentration of bromine could be calculated using the number of counts from the bromine region of interest in the XRF spectrum:

[Bromine] (in ppm) = = 0.000364(counts) - 12.420864

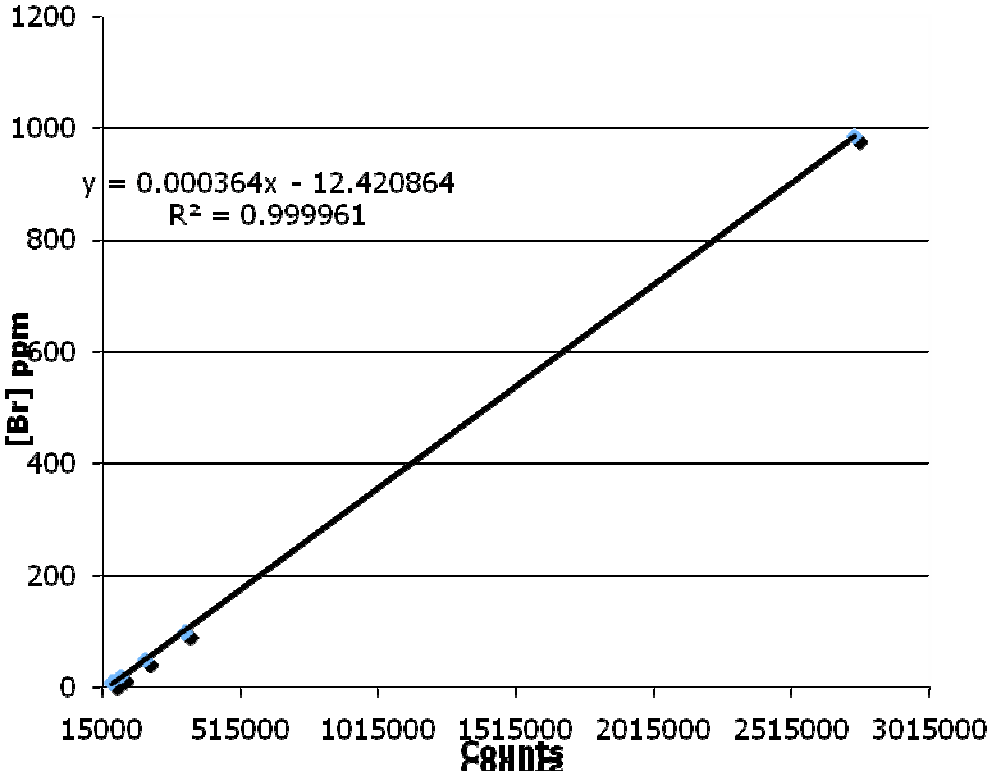

Figure 4. Bromine Calibration

In order to determine the limit of detection for bromine, glucose was used as a sample blank since it can be considered to be representative for the foodstuffs that were investigated. The average background counts for five samples were 25511 counts and the standard deviation (σ) was found to be 518. Using a value of 5σ as a basis for detection of a peak above the background gives a detection limit of 0.94 ppm. Since the maximum concentration limit for bromine content is 125 ppm, any sample with counts greater than **377,472** would be deemed to have an unacceptable concentration.

ANOVAs were conducted comparing the two groups of interest in this research, those being manufactured items made in the United States and those manufactured in

countries other than the United States with values on **Table 7**. The two groups were compared once for bromine content and once for lead content.

No significant statistical difference was found between these two groups for bromine or for lead content based in a one way ANOVA analysis. However the graphic representation of the data shows outlying samples that were extremely high in elemental contaminants.

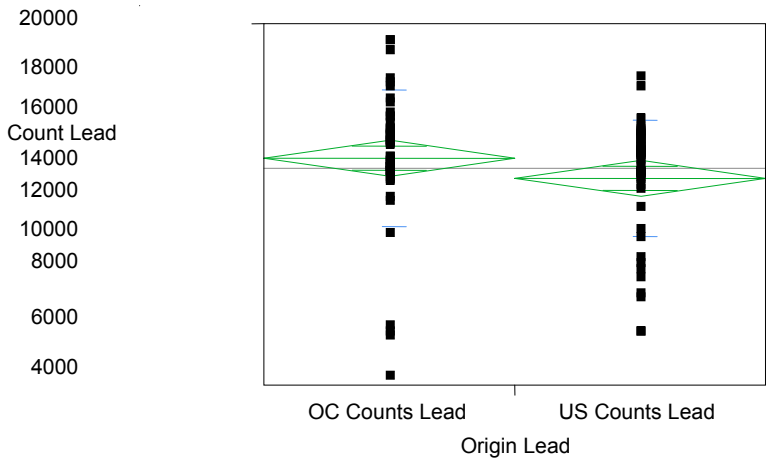

Figure 5. One-Way ANOVA of Pb Comparing Means of US and OC Groups

The very limits of modern detection are at play in this survey type research. The technology does not exist to make calculations that are much smaller than shown by these data as with particularly the lead measurements were selected at 0.1 ppm of one tenth of

one part per million as this is the allowable level of lead in food stuffs. The p value from this one way ANOVA was 0.1271 and much higher then the established 0.05 alpha level therefore we fail to reject the null that there was a significant difference between the two groups in question of US and OC. The p value generated by this ANOVA was 0.1271 and while this value is much greater than the established .05 α. Based on this ANOVA which only looks at the means of the two groups in question, the means show no significant difference, therefore refereeing only to this ANOVA we fail to reject the null hypotheses H_{01} and H_{02} as both of these hypotheses predicted differences would be present in products based on country of origin.

Table 7

Analysis of Variance for Pb Content One-Way ANOVA

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Origin Lead	1	18463350	18463350	2.3671	0.1271
Error	98	764414173	7800144.6		
C. Total	99	782877523			

A one tenth of one part per million is an incredibly tiny increment for analysis. It in effect means if the sample were to be divided into a million parts from the original size and then into ten more equal portions only one to these final divisions would be found by

analysis to be the elemental toxin lead. The United States government has established this extremely low amount of lead in food stuffs based on the detrimental effects on the physiological systems that have been shown to be so severe. With current modern technologies this value it deemed feasible to achieve.

Levene's test of variance was conducted on the same data set for lead. As reported by Levene's test (1997), it is utilized to assess if the variance in different samples is equal. Levene's test showed a p value of 0.9224, a value that indicates that variation is close to the same within the two groups tested. Statistically a value arrived at of 1 would indicate the two groups in question are perfectly equal, and this is considered a statistical impossibility. When Levene's statistic is a value less than .05, this means the variation in the data is very different and therefore a test called a Welch ANOVA as explained by Ott and Longnecker (2001) should be used. Levene's statistic further tests the premise that the populations in question have equal variances. If the Levene's test were to be found less than the set alpha level of .05 then it can be concluded that the difference in variance is unlikely to have occurred based solely on random sampling error. Here the value for Levene's was well above the level of .05 therefore we fail to reject this premise.

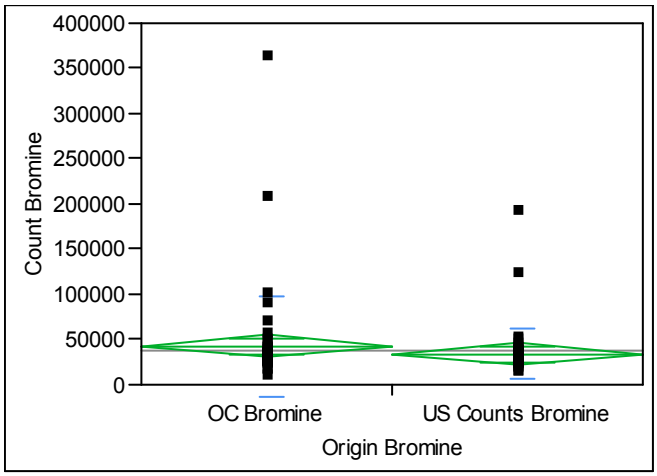

Figure 6. One-Way Analysis of Count Bromine by Origin Bromine

The p value obtained from this ANOVA was 0.3191. This is a p value greater than .05 as established to be the probability level for this study. The probability level chosen for a study established the point of decision on all hypotheses. A Type I error is committed when research rejects a null hypothesis that is in reality true. The value of 0.3191 is much greater than .05; therefore there is not enough data to reject the null. This probability level allowed this study to report with 95% confidence that the means of the two group's tests are statistically the same.

Table 8

Analysis of Variance for Br Content One-Way ANOVA

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Origin Bromine	1	1895479076	1.8955e+9	1.0028	0.3191
Error	98	1.8523e+11	1.8901e+9		
C. Total	99	1.8713e+11			

It was determined after thoughtful examination of this data that Levene's test would be run on the same set of data as this test does not address the observation that the data sets are skewed. The results of Levene's test for bromine further reflected that there was not enough evidence in this data to reject the premise of unequal means as the value obtained from Levene's was 0.1057 as it measured variance. It can be concluded that the variance of the data set of OC group equals the variance of the data set of the US group as Levene's test measures variance between groups of data.

While every attempt was made to choose random samples from the wide variety of possible food stuffs available, a few samples tested very high for elemental contaminants and were well above the mean of groups. This would indicate that the companies both in the United States and in countries other the United States that manufactured these products are currently exercising excellent practices related to food safety and elemental toxins.

After examination of the data from these initial results, it was determined to be feasible to ascertain if there is a significant difference between the manufactured products from the United States and those manufactured in countries other than the United States. This was based on the evidence that was numerically obtained indicating some statistical difference might be present, but not in the current clusters of data sets. Therefore there was some indication that this data should be disaggregated into sub groupings and further analyzed.

Careful consideration was given to the sub groups that most logically fit into the entire scope of this study and how to achieve this division. While samples were initially being purchased, it was apparent that some were already divided by the title given to the food product as displayed on the labeling. The samples were subdivided into the categories of candy, cookies, drinks, finger foods, fruit snacks and those that were very unique or monolithic clustered into a group called others.

Another logical sub division was determined to be country of origin as the initial one way ANOVA clustered all of the samples as manufactured in a country other than the United States, and knowing which particular country as indicated on the manufacturer's label was very possible. It had been observed that many samples were manufactured in China and in Mexico respectively. There were other countries represented in this study; however none had a large cluster of items but only a few or one, such as Ireland, or Italy with one item each. It was considered that a comparison of elemental toxins as compared between China and Mexico would be possible along with large groups combining countries of origin that were all contained within the European Union. Therefore specific sub groups within the large cluster of samples indicated as manufactured in a country other than the United States were considered and sub divided for analysis. These groups were decided to be Asia, China, European, Latin America, Mexico, and a category called other that included any country of origin that did not fit well within aforementioned groupings. This data set would also include the large and initial data set of items manufactured in the United States.

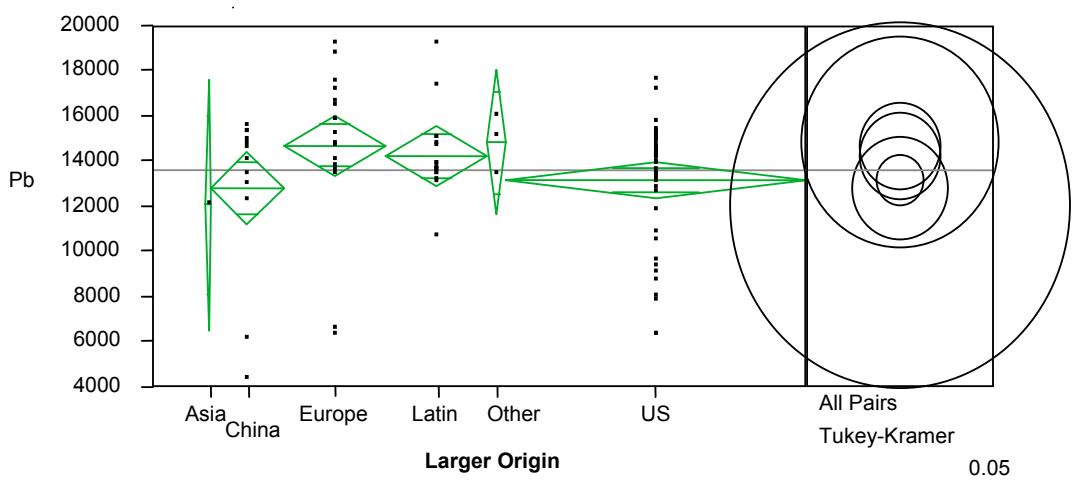

Figure 7. One-Way Analysis of Pb by Larger Origin in ROI

The p-value of 0.3115 obtained in Figure 5 from a one way ANOVA is a much larger value than .05 α; hence it has been concluded that there is insufficient data to reject the null hypothesis of equal mean lead values between countries of origin. The tests for equal variances, Levene's indicate a value of 0.2865 and therefore the null hypothesis of no difference in variances among the sub group "Larger Origins" cannot be rejected with the current data set. The p value for Levene's shows 0.2865 and is greater than .05, so therefore the decision was made to not use Welch's ANOVA.

The width of the diamond graphic representation indicates sample size of each sub group. To interpret the above data set, it was noted that the United States sample depicted a very large and wide triangle indicating all fifty samples in this sub group. The sub grouping of Latin America had only a few samples as these were the ones found from this origin when the random search for possible sample occurred. This could indicate many possible reasons for this disparity in size of sample sets. A few, but not all reasons might be trade agreements between the United States and certain regions of the world,

and regional specific commodities based on climate and cultures.

The Tukey-Kramer HSD test compares paired groups within the data set. As all circles represented on the graphic are interconnected, this test also shows no significant difference between any data sub set. The specific number of each sample in this sub grouping along with the means of each set are provided in **Table 9** for clarity to portray a clear depiction of the data sets represented. When dealing with small data sets, great caution must be exercised as, the smaller the data set, the less likely it is to be a good representation of the population in question. However this survey type study initially looked at only two large data sets. Only after the one way ANOVA was conducted showing no difference was it determined to run further analysis.

Table 9

Means of On- Way ANOVA of Pb by Larger Origin in ROI And Tukey-Kramer HSD Grouping

Level	Number of samples from each country	Grouping A or B	Mean
Asia	1	A	12049.0
China	12	A	12788.6
Europe	12	A	14343.8
Latin America	5	A	13755.6
Mexico	12	A	14430.5
Other	8	A	15256.9
United States	50	A	13173.3

Therefore the sub grouping of country of origin showed no significant differences when the edible manufactured samples were further analyzed. Careful consideration was further given to any other sub group that most logically fit into the entire scope of this study and how to achieve this division. While samples were initially being purchased, it was noticed that some were already divided by the title given to the food product on the labeling. Therefore samples were further sub divided into the categories of candy, cookies, drinks, finger foods, fruit snacks and those that were unique or monolithic clustered into a group called others. This new sub division was analyzed utilizing a one way ANOVA and a pair wise Tukey-Kramer HSD. This trial showed a much different result as indicated on the attached graphic. It was noted that one sub grouping of finger foods was significantly different from the others in elemental lead content.

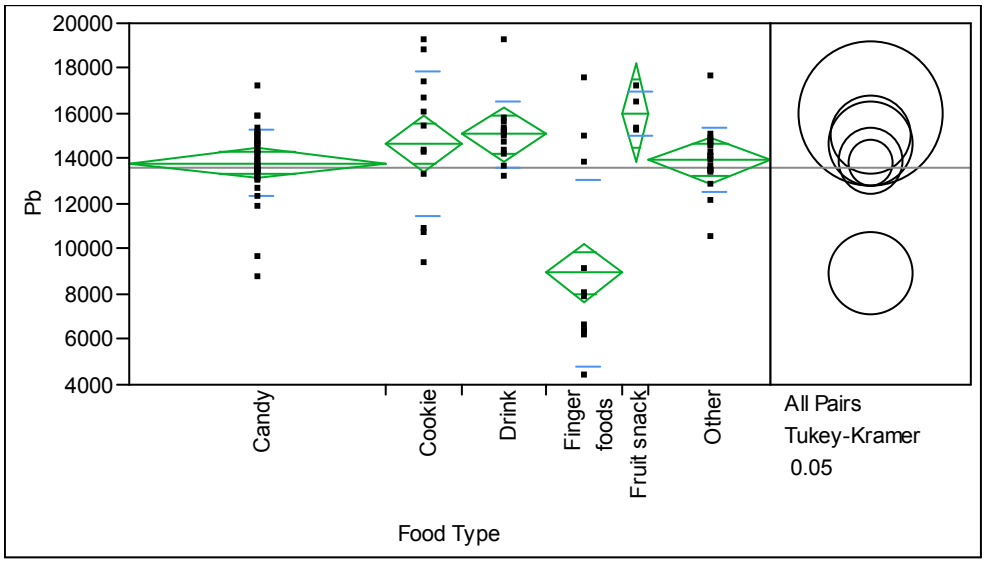

Figure 8. One-Way Analysis of Pb by Food Type

The resultant p value from this ANOVA was < .0001 which is a value well below the .05 α level, and so indicated that a level with 95% confidence, these sub sets are different form one another.

Table 10

Analysis of Variance for Pb by Food Type

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Food Type	5	329811906	65962381	13.6873	**<.0001***
Error	94	453009946	4819254.7		
C. Total	99	782821852			

*** Significant at p≤ .05**

Levene's test of variance was run resulting in a value of < .0001 also indicating that with 95% confidence, the variation of these data sets were different. If one variance for food type is found to be statistically different as compared to the others, the Welch ANOVA was used for the significance test on means, indicating that at least one mean is different from the others. The Tukey-Kramer test indicates that the mean lead values for "finger foods" differ from all other mean values at the 95% confidence, having a much lower mean value than the other categories. It can be stated then with 95% confidence that this data shows that the "finger foods" sub group has a lower mean of the elemental toxin lead than analyzed for other food items in this survey. Additionally it was observed that the entire sub group called fruit snacks were above the mean for this data set. While fruit snacks was a very small sub set of four samples total and great caution must be exercised with small sample size, this might indicate more research should be undertaken on the sub grouping fruit snacks alone with a larger sample size.

Table 11

Means of One-Way ANOVA of Pb by Food Type in ROI and Tukey Kramer HSD Grouping

Level	Number of samples from each food division	Grouping A or B	Mean
Candy	40	A	13815.700
Cookie	12	A	14653.083
Drink	13	A	15071.538
Finger Foods	12	**B***	**8934.000***
Fruit Snacks	4	A	16006.500
Other	19	A	13930.053

*** Significant different subgroup at p≤.05**

Data levels not connected by the same letter are significantly different and as the sub group of finger foods is in group B as opposed to all other groups belonging to A this shows there are significantly differences based on a level of .05 α. Therefore the sub grouping of food type showed significant differences when the edible manufactured samples were further analyzed. A further analysis of a Welch ANOVA was run and yielded $p = 0.0004$; much lower than the .05 alpha level chosen. The Welch ANOVA is used as a significant test to compare means. This would indicate at least one mean is different from the others in this sub grouping. These values were significantly below the mean values for lead in ROI counts; therefore the sub groups designated as "finger foods" were extremely low in any lead, if indeed any detectable lead was within these samples. A sample named "Blank" was analyzed to establish background scatter from the XRF and contained only distilled water, this sample resulted in a value of 14843 as a ROI count value.

When the means of the samples are compared to the blank sample only the fruit snacks indicate some difference might be shown. However statistically there was calculated to be no significant difference. In conclusion the edible samples for this survey study did show a difference; however that difference fell into the category of extreme purity within the category of finger foods.

Potential future studies could gather a much larger sample of the sub set fruit snacks and analyze for elemental contaminates. However the small sample size for this sub group and the resulting data calculated prohibits any positive finding of levels of lead above United States governmental standards of 0.1 ppm in edible food stuffs.

The other elemental toxin of concern found by analysis by the XRF was bromine. A one way ANOVA was conducted to determine bromine levels also reported in the unit ROI as previously reported and the p value was shown to be 0.319. This was deemed to be sufficient evidence to reject the H_{01} and H_{02} previously discussed, indicating that the means of the two groups were the same at a 95% confidence level. These values are given on **Table 12** and depicted in **Figure 9** below.

It was determined to keep the same sub groupings and run further analysis to see if this would result in variations for the elemental toxin bromine. The first sub grouping was by country of origin as this logical grouping was clearly given on the packaging for the individual product in question.

This would also provide consistency between the two toxins of interest being lead and bromine with the same divisions and test administered.

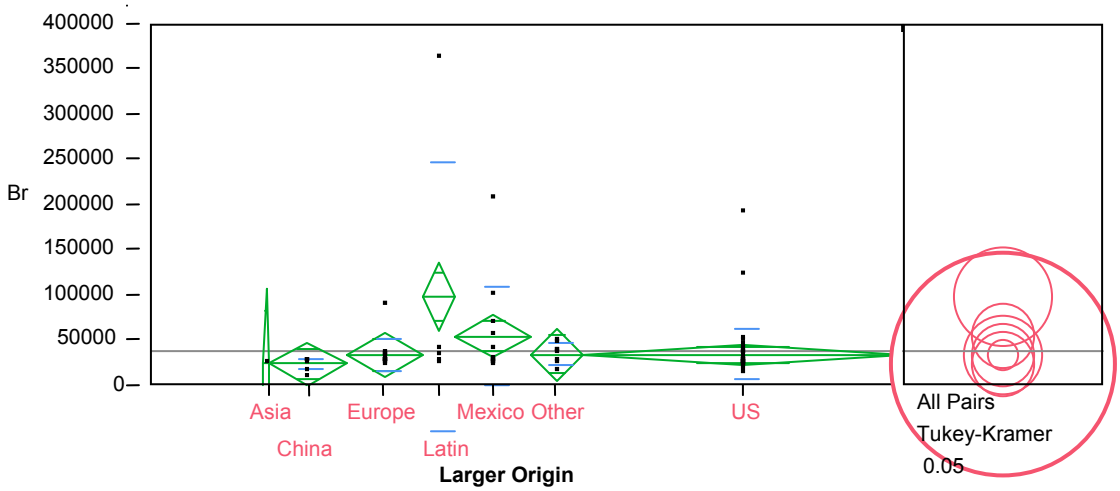

Figure 9. One-Way Analysis of Br by Large Origin

The one way ANOVA resulted in a p value of 0.0355 or a value less than the established .05 alpha. Therefore we must reject the following null hypothesis, H_{01} there will be no significant level of elemental toxins detected in products that were manufactured in the United States but significant levels of elemental toxins detected in products manufactured in countries other than the United States. Additionally, H_{02} there will be no significant level of elemental toxins detected in products manufactured in countries other than the United States but significant levels of elemental toxins will be detected in products manufactured in the United States will be rejected based on these statistical tests.

With a p value as stated above, it is determined that statistical differences are present at a .05 alpha level, when the data were divided into subgroups however it was noted that the Tukey-Kramer statistic showed no distinction between pair wise comparisons. This result is due to this test being very rigorous. The nature of this survey type study involved elemental toxins in children's food stuffs. Based on the sensitivity of this surveys outcome it was determined to err on the side of rigor and so the Tukey-Kramer statistic was chosen. The small sample sizes that occurred during division of some subgroups, such as those manufactured products from Latin America is a very small number, this sample size then resulted in the Tukey-Kramer test showing no differences in groups.

The Welch ANOVA was conducted also to test for equal means and resulted in a value of 0.0437 or a value less than the established .05 alpha level.

Given the significant Levene's value of <.0001 and the Welch ANOVA, both

suggest that the null hypothesis of equal Bromine means across "Larger Origin" can be rejected. The Tukey-Kramer honestly significant difference table indicates that the Latin America sub grouping has a higher mean value for Bromine than either the US or China. However, at 95% confidence level, the US and China do not have statistically different mean bromine values as they are placed within the same groups of B by the Tukey-Kramer HSD grouping from the analyzed data.

Table 12

Means of One-Way ANOVA of Br by Larger Origin in ROI and Tukey-Kramer Grouping

Level	Number samples from each country of origin	Grouping of A or B		Mean
Latin America	5	**A***		97503.400
Mexico	12	A	B	54163.250
Other	8	A	B	33942.500
United States	50		**B***	33636.080
Europe	12	A	B	33301.750
China	12		**B***	23758.417
Asia	1	A	B	23427.000

*** Significantly different from other points of origin at $p \leq .05$**

In addition to the elemental contaminant lead, the bromine analysis for this study was further sub divided by food types. In order to maintain consistency samples were again sub divided into the categories of candy, cookies, drinks, finger foods, fruit snacks and those that were unique or monolithic clustered into a group called others.

The food type sub division was analyzed utilizing a one way ANOVA and a pair wise Tukey-Kramer HSD. Again, the Levene's test resulting in a value of < .0001 indicates sufficient evidence to reject the null hypothesis of equal variances, and the Welch ANOVA of <0.0029 suggests that at least mean bromine value is different from the others for the factor "Food Type", as earlier analysis of with "Fruit Snack" and "Candy".

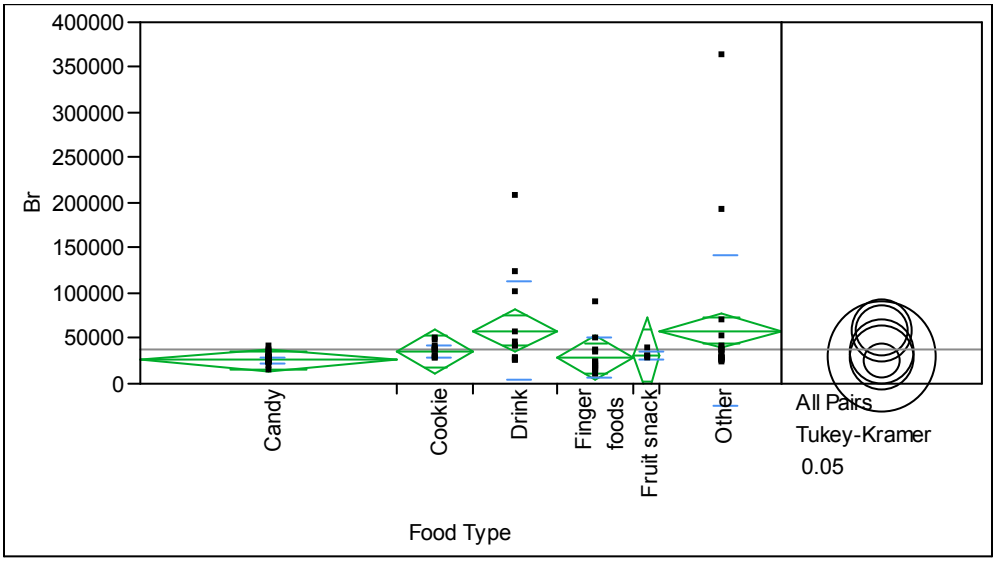

Figure 10. One-Way Analysis of Br By Food Type in ROI

The Tukey-Kramer HSD does not indicate any significant multiple comparisons, however. This may be due again to the Tukey-Kramer being conservative when sample sizes differ.

Table 13

Means of One-Way ANOVA of Br by Food Type in (ROI) and Tukey-Kramer HDS Grouping

Level	Number sample size from food Sub-grouping	Grouping A or B		Mean
Drink	13	**A***		58854.923
Other	19	**A***		58725.895
Cookie	12	A	B	35629.333
Fruit Snack	4	A	B	30602.750
Finger Foods	12	A	B	28506.083
Candy	40		**B***	25650.675

*** Significantly different from other food sub groupings at $p \leq .05$**

A further analysis was conducted of a student's t test due to the sample size being so small in some sub groupings. The student's t test specifically is a distribution that is useful when for multiple reasons when the sample size is very small and differences would be rejected by other statistical tests. This test might have multiple specific examples where its use is valid. There might be a very rare medical condition whose medical treatment is being studied and very few persons afflicted are available for study. In this survey as samples of manufactured products were randomly purchased one of the

initial parameters was country of origin being the United States or a country other than the United States and then imported. The values in **Table 14** given in bold type font were found to be different when pair wise groups were analyzed with this test for bromine content. The Student's t least square means indicates for example the sub group of "Candy" was found to be different from the subgroup "drink."

Table 14

LS Means Differences Student's t

0.050 t= 1.98552
LSMean[i] By LSMean[j]

Mean[i]-Mean[j] Std Err Dif Lower CL Dif Upper CL Dif	Candy	Cookie	Drink	Finger foods	Fruit snack	Other
Candy*	0 0 0 0	-9978.7 13825.1 -37429 17471.4	***-33204**** ***13409.8*** ***-59830*** ***-6578.7***	-2855.4 13825.1 -30305 24594.7	-4952.1 22026.9 -48687 38782.9	***-33075*** ***11703.3*** ***-56312*** ***-9838.1***
Cookie	9978.66 13825.1 -17471 37428.7	0 0 0 0	-23226 16814.9 -56612 10160.8	7123.25 17147.9 -26924 41170.9	5026.58 24250.8 -43124 53177.2	-23097 15488.2 -53849 7655.61
Drink*	***33204.2**** ***13409.8*** ***6578.7*** ***59829.8***	23225.6 16814.9 -10161 56612	0 0 0 0	30348.8 16814.9 -3037.6 63735.3	28252.2 24016.5 -19433 75937.5	129.028 15118.7 -29889 30147.5
Finger foods	2855.41 13825.1 -24595 30305.5	-7123.3 17147.9 -41171 26924.4	-30349 16814.9 -63735 3037.59	0 0 0 0	-2096.7 24250.8 -50247 46053.9	-30220 15488.2 -60972 532.356
Fruit snack	4952.08 22026.9 -38783 48687	-5026.6 24250.8 -53177 43124	-28252 24016.5 -75938 19433.2	2096.67 24250.8 -46054 50247.3	0 0 0 0	-28123 23107 -74003 17756.4
Other*	***33075.2**** ***11703.3*** ***9838.14*** ***56312.3***	23096.6 15488.2 -7655.6 53848.7	-129.03 15118.7 -30148 29889.5	30219.8 15488.2 -532.36 60972	28123.1 23107 -17756 74002.7	0 0 0 0

*** Student's t least square means subgroups found to be different**

It was determined that a two way ANOVA was not possible from the current data that had been randomly collected for this study as categories are different. This was unknown until this data had been divided into logical sub groupings for further analysis. This difference was arranged and displayed in a data table to show this difference,

Table 15

Food Type in Rows and larger Origin in Columns Spread Sheet to Determine A Two-Way ANOVA Was Not Feasible

	Asia	China	Europe	Latin America	Mexico	Other	United States	All
Candy	0	7	3	3	5	2	20	40
Cookie	0	0	0	0	2	4	6	12
Drink	0	1	2	1	3	0	6	13
Finger Foods	0	2	3	0	0	1	6	12
Fruit Snacks	0	1	0	0	0	1	2	4
Other	1	1	4	1	2	0	10	19
All	1	12	12	5	12	8	50	100

In summation for lead content the only statement that can be made at a 95% certainty for this data from this study is that the category of "finger foods" has a lower lead content than any other sub grouping of food items analyzed.

Additionally the sub group of edible manufactured samples from Latin America as divided by country of origin within the large cluster of samples manufactured in countries other than the United States shows that sub group is higher in bromine at a 95% level of certainty than any other sub group. It was determined after all sub groups were compared there was no significant difference between United States samples and those from China.

The most startling of these findings were from the metal harmonica manufactured in a country other than the United States that tested extremely high in lead content. While this musical instrument is not edible, it is specifically designed to be in close oral contact, or taken into the mouth cavity of the small child playing it. The harmonica and the mouth harp were analyzed utilizing the hand held Niton XRF.

As only one item that was not edible was tested in this study it was not included in the data inclusive of edible items but listed separately below.

Table 16

Levels of Lead Detected by the Hand-Held Niton XRF in the OC Harmonica Values Given in (ppm)

Trial	Trial	Trial	Trial	Trial	Average
1	2	3	4	5	
319	200	100	200	200	203

The United States government allows only 0.1 ppm of lead to be present in edible food items or non edible food items that are meant to come into close oral contact with a small child or an infant. This harmonica is packaged with a booklet of musical compositions for small children in preparation of their learning to play musical notes. There is a photograph of a small child on the cover of this booklet. This harmonica was purchased when found on an aisle where toys are prominently displayed in a large nation wide store. This finding then of on average of 203 ppm is extraordinarily high for the elemental toxin lead. The "mouth harp" manufactured in the United States found as the best fit match for the harmonica was also tested 6 times using the hand held XRF and every trial showed 0.00 ppm for lead content.

Significant differences as previously explained within two sub groupings of edible manufactured samples were found in this survey type study for the elemental toxins bromine and lead. Additionally the one pair of samples that were non edible but specifically intended to come into close oral contact by a child was very significantly different in lead content. The following hypotheses were made at the onset of this survey. They are incorporated below with a determination as to their rejection or failure of rejection based on the completion of the data analysis.

H_0 There is no significant level of any elemental toxin detected in any sample tested from sample groups of products.

We reject this null hypothesis as there were significant levels of elemental toxins found in some samples from both groups.

H_{01} There is no significant level of elemental toxins detected in products that were manufactured in the United States but significant levels of elemental toxins are detected in products manufactured in countries other than the United States.

We reject this null hypothesis as one United States sample for lead content was shown to be above the standards for allowable lead content of .1 ppm with 95% confidence.

H_{02} There is no significant level of elemental toxins detected in products manufactured in countries other than the United States, but significant levels of elemental toxins are detected in products manufactured in the United States.

We reject this null hypothesis as multiple samples analyzed for lead content were shown to be significant for standard lead contents of .1 ppm for lead.

H_{03} There is no significant level of mercury found in any sample tested, but other elemental toxins will be detected at significant levels, specifically, lead and bromine.

We fail to reject this null hypothesis as no significant levels of mercury or bromine were found in any sample however significant levels of the elemental toxin lead are detected in both groups.

CHAPTER V

CONCLUSIONS, DISCUSSION AND RECOMMENDATIONS

Conclusions

After careful examination and interpretation of the resultant region of interest (ROI) counts displayed by the X-ray Fluorescence Spectrometers (XRF) of all samples, it has been determined that there are significant levels of one of the elemental toxins of interest (lead), contained within some samples. In addition, when data were calculated and statistical values obtained from multiple tests at a .05 alpha level of significance of sub groupings, differences between some logical clusters were found at a 95% confidence level.

Discussions

The Elemental Toxin Mercury

No mercury levels were detected in any sample analyzed. Inestimable and minuscule amounts could have been present; however background interference and scatter from the matrix effect negated any indication at this toxin. Many samples had unusual shapes and surface abnormalities as the raw product was removed from individual packaging and broken into sample size pieces. These unusual surfaces

abnormalities could exacerbate the matrix effect; however this study has concluded from XRF readings that no measurable mercury was found within any sample.

The Elemental Toxin Lead

Negligible lead was detected in all except 9 samples tested, as compared to the water based and sugar solution control samples run as a comparison. All controls were calibrated to be as close as possible to the 0.1 ppm value established as being significant for lead content by the United States government within food stuffs.

The United States government food and drug agency (FDA) has established that 0.1 ppm of lead or less is an acceptable quantity of lead in food stuffs with current technologies. Lead in many cases is inexorably bound to calcium and occurs in this way within systems in nature. The uptake of lead into biological systems and its storage with calcium in the formation of shell and bones and calcium carbonate formations is widely accepted. These natural sinks of calcium are the main reservoirs by which calcium is procured for industry usages. Acknowledge that calcium is a nutrient necessary for life negates a zero tolerance for lead as complete separation cannot currently be feasible as is related to manufacture food items.

The quest for zero amounts of lead in food stuffs especially those specifically intended for consumption by small children and infants is a complex issue and requires perspective. As modern technologies including the use of an XRF push the envelope of detection, the obvious question becomes, how low of an amount of a toxin is currently feasible. Could zero elemental toxins be achieved when extraordinary care is taken during production of food stuffs, or is zero impossible to achieve? Any company, in

order to mass produce a reasonably priced product, must balance rigorous safety with economic reality and this balance then becomes the bottom line of their feasible business practices.

Scientific research wears the mantel of proof that no harm is done to the consumer and this levies the weighty responsibility of understanding elemental toxins squarely on scientific shoulders. Currently, acceptable levels of each toxin are established by the United States government through the FDA whose levels have been attained by scientists through rigorous and time consuming research. With consideration toward complex myriads of interwoven environmental awareness that address best available practices, the United States government has established such levels for a multitude of toxins. This methodology explains the rationale for the allowable levels of incredibly tiny increments of lead and its subsequent findings in trace amounts in some samples within the limits in this research.

Four standards were created serving as controls for lead content that were analyzed and subsequently facilitated a comparison to the one hundred total edible samples analyzed for this study. Additionally one pair of non edible samples was analyzed that were specifically intended for close oral contact by a young child. These four standards were carefully created to be representative of different background solution possibilities within this study. Two standards were comprised of quantified lead standard and distilled water, while another two were quantified lead standard and sterile glucose solution. All four standards were calculated for lead content. The four standards were then analyzed utilizing the XRF for the same length of time as all samples, that being one hour of read time and a total of two hours of run time and their (ROI) region of

interest counts obtained. The four standard values were averaged and the resultant mean derived. The average background count for five samples was 13648 counts and the standard deviation (s.d.) was found to be 555. Using a value of 5s.d. as a basis for detection of a peak above the background, any sample with counts above **16424** would be considered positive for lead content. This corresponds to a detection limit of 1.49 ppm.

Calculations were conducted and yielded a standard deviation of considered significant for lead levels above the 0.1 ppm established by the United States government as the acceptable level of lead in products for consumption. Five standard deviations resulted in a numerical value of 16424 for (ROI) count which will be used as the reference point for this study to report significant lead was found within any sample. The 5 sigma value of significance was an extraordinary measure to ensure accuracy in reporting results, as this area is referred to as the region of rejection statistically within the outer realm of any sample of a population to report with 95% confidence or a .5 alpha level we chose this high standard. While any value above the mean was also considered a decision to err on the side of great caution, this measure was selected due to the weighty nature of this study. This study also pondered the matrix effect and how best to avoid presumptuous conclusions. As discussed earlier the matrix effect can confound results when XRF technology is utilized. This effect which might tend to scatter emitted light from a sample cannot be neglected when reporting conclusions in any viable research using an X ray Fluorescent Spectrometer. Additionally the matrix effect can affect data when results read are confounded by the difference in the concentrations of interfering elements.

We chose only two non edible samples which were the child's harmonica and the mouth harp. These were each analyzed for a total of six times for 30 seconds each in different areas along their surfaces with the hand held Niton XRF.

All samples that were edible products were shown to be higher than 5SD above the mean for standards were reanalyzed utilizing the hand held Niton XRF. All were shown to have 0.00 ppm for lead which was due to the limitations of this machine. The manufacturer states that the hand held Niton is only accurate to six ppm or greater in any sample. The amounts of lead that would be significant are of a much lower level as allowed by the Food and Drug Administration (FDA) being 0.1 ppm in food items. The Niton read 0.00 ppm for lead when used for analysis of the seven samples suspected of significant lead levels.

This study analyzed one hundred samples that were meant for oral consumption and two that were intended for close oral contact. The first of these two non edible samples consisted of a child's harmonica, a musical instrument intended to be held in the mouth of the child and by expelling air causing a vibration and resulting musical tones. This harmonica was manufactured in a country other than the United States. As the random purchase of samples occurred in different stores for items that fit the parameters of this study a child's harmonica was observed and as this item is specifically intended to be placed in the mouth of the child it was chosen to be analyzed for elemental toxins. This research encountered great difficulty when a search was made for a similar harmonica made in the United States. After several months and many enquiries, it was determined that there are no harmonicas currently manufactured in the United States. It was discovered that in years past, there were companies in the United States that

manufactured harmonicas. However all of these were no longer currently manufacturing this product. An appropriate substitute was made of a musical instrument called a "mouth harp" that is commonly used in bluegrass bands and similar formats. This instrument is also made of metals and also held in the mouth of the child playing it. It was determined that this musical instrument was manufactured in the United States and a decision made to accept it as a best fit or a suitable comparison to the harmonica that had been manufactured in a country other than the United States.

The second instrument of each set was set aside as a control for future reference if such a need arises. This explanation is included to bring awareness that this research was undertaken with the greatest of care and precision that was possible in selection of best fit samples tested.

The hand held Niton showed highly significant levels of lead were contained in the harmonica manufactured in a country other than the United States. The harmonica had been disassembled to facilitate reaching all of the metal surfaces of the instrument. The original thickness of the instrument prohibited its analysis by the large XRF at Oklahoma State University as a safety latch on the device must securely fasten before the X rays are emitted into any sample. When a small child would play an instrument such as a harmonica the outer metals along with the metals layered inside that are exposed along the edge of the instrument as both are placed inside the child's mouth. The external metal of the harmonica was found to be plated with chromium. The internal layer of metal, whose outer edge is placed inside the child's mouth, which appeared to be a bronze color, tested positive for lead content. Six readings from different areas on this exposed edge of

internal metal parts showed the levels of lead as recorded by the hand held Niton and displayed in Table 16.

The mouth harp manufactured in the United States was also analyzed with the hand held Niton multiple times and in multiple places along the surface of the metal made to be contained in the mouth of the child playing it. Every reading in every position tested for lead by the Niton was 0.00 ppm for lead content in the mouth harp.

The Elemental Toxin Bromine

No samples were showed to contain significant levels of the elemental toxin bromine at the current level allowed by United States regulation of 125 ppm. It should be noted that several of the samples tested were very high in bromine content however did not meet the 95% level of significance established by this survey. The value of ROI count found to be significant for bromine levels was **377,472** several samples had levels almost to the high limit. Sample OC50 imported chicken soup mix was determined to have a ROI count of **363,191** and a sample of imported baby formula a count of **207,767** while both of these values are within current United States standards they are high values.

Bromine as detected by an XRF occurs in many different forms including organic molecules, salts and additionally as an element within a diatomic state referred to as bromide and in solution as an ion called bromine. All of these species of bromine are possible suspects in the detection by the XRF of the bromine peaks indicated by this analysis. The idea of multiple forms of an element having dynamic and diverse interactions with the human body requires explanation. Bromine can be analogous to a more common element that would serve to set the focus for comparison of a foundation

of these statements. Chlorine, a similar element to bromine located just above it on the periodic table, can serve as such an example. Chlorine can be a nutrient essential for human health and vital to the functioning of many systems within the human body. Chlorine is also found naturally in ocean waters as sodium chloride commonly referred to as table salt. However if chlorine is isolated it becomes a highly poisonous green yellow gas referred to as gaseous chloride at STP (Standard Temperature and Pressure). While all of these aforementioned species would be detected as chlorine with an XRF, some within the correct dosage in the human diet are essential to life and one is a deadly toxin. Bromine to some extant is a similar element to chlorine with some comparable properties. The technology that allows the detection of an elemental peak does not allow the actual determination of what form the bromine is in within these samples. While the two elements, chlorine and bromine are similar, they have some profound differences.

One of the most consequential is that bromine has been shown by the combined medical community to have no useful role even as a trace nutrient in human physiology. Additionally the human body's reaction to bromine is as a toxin or is one of mistaken identity as the body mistakes bromine for chlorine. A unique difference between bromine and chlorine is that, at STP, bromine exhibits as a reddish brown liquid due to increased dispersion forces more tightly binding this element than chlorine, making it one of only two liquid elements at STP. Bromine, whose name in Latin literally means stench, refers to its foul odor when in this liquid elemental state. Bromine has a much larger mass per mole than chlorine facilitating a greater density which contributes to bromine's interference with bodily functions and exhibits as bromine poisoning. Bromine

has been classified as a xenobiotic, meaning it is not required by any body system, tissue, or life processes.

Research has shown that within all biological life on the planet, including flora and fauna, only certain types of red algae and some species of mollusks use trace amounts of bromine. These primitive life forms concentrate bromine from sea water and use it as a defensive ink possibly to dissuade predation. The first recorded use by people of bromine was when ancient civilizations extracted this reddish chemical from these primitive mollusks to create the variety of royal purple dyes valued in regal attire.

A medicinal usage of bromine is usually listed as sedation as its profound effect on the brain and nervous system serves in essence to shut down the nervous system's function causing a wide range from calmness to sleepy stupor.

World wide it has been scientifically accepted that bromine based salts naturally occur in the ocean. Additionally a multitude of different research studies in the past have established that tiny amounts of bromine in the diet of an adult have been shown to cause no long term toxicity or physiological harm. However newer research, (Betts, 2008) currently has establish negative effects on the endocrine system where bromine ions might interferer with the uptake of iodine ions and their critically important roles within hormone feed back loop systems. In most cases, especially when adults of full stature consume food stuffs that contain very tiny amounts of the element bromine, the effect is described as a mild calming symptom to no effect at all. However if the dosage is larger based on concentration in the blood a daze or stupor occurs and hence a sedative effect is observed. Toxic levels of bromine have been established and accepted by the medical community based on concentrations of this element per amount of volume of blood.

Some research has indicated that bioaccumulation might occur with particular fat soluble toxins and bromine is one toxin of interest in this arena. The dose then makes the poison with bromine as with most toxicants. With continual doses from multiple venues including food stuffs, bromism looms as an omnipresent possibility especially to infants and young children.

Ellenhorn's (1997) medical toxicology, a reference for physicians in cases of poisoning has established specific levels of bromine in blood and ranked different subdivisions of this toxin under the heading of bromism, or bromine poisoning. These levels are based on the concentration of milligrams of bromine per deciliter of blood of the victim.

The different levels established are first, the lowest level or so called therapeutic level, referring to the medical community's ability to interact with this level of bromine and through curative or healing powers negate all symptoms of poisoning from the patient. The therapeutic level has been established as having less than 50 mg/dL of bromine in the victims' blood.

The next level of poisoning established by Ellenhorn, (1997) is described as possible toxicity; this range is established when bromine is found between 50-100 mg/dL of blood. At this level the adjective, possible would tend to describe the potential for the intervention by medical treatment to facilitate wellness. However, if no treatment were administered of a period of time, toxicity or poisoning could occur. Toxicity is described as the degree to which a poison is toxic or injurious to the tissues of the human body.

The higher and more severe category for bromism is quantified as, usually serious toxic with the amount of bromine found in these cases described as between 100-200

mg/dL of blood. The injection of the new adjective, "serious" ranks this level of poisoning as a much more elevated threat of damage occurring.

If the amount of bromine in the blood is measured to be an extremely high level of 200 to 300 mg/dL Ellenhorn, (1997) describe the toxicity as resulting in possible coma where the body systems in effect lapse into a deep unconscious state.

The final and most severe level of bromism is defined when there is as a level of over 300 mg/dL of blood. This level is so severe that it is described as possibly fatal.

Along this continuum of poisoning and the resultant effects, special note should be made that this study had as a focus only those manufactured products that any prudent and reasonable adult would feel that a child six and younger or an infant should consume or come into close oral contact with. This special subgroup within the population is accepted as especially sensitive to toxins. The United States government has quantified this by advising that a ten fold increase of safety and awareness should be engaged when edible products have such a probable consumer. This increase of safety and awareness is based on the smaller body size ratio to the possible toxicant of interest and the accepted phenomena that incredible growth spurts of the developing body systems occur within early childhood years. If a toxicant is finding access into the body at this crucial juncture of development medical research leads us to the conclusion that the potential for prolonged injury is much greater. These include but are not limited to the development of the nervous system and developing brain.

Numerous research studies have established that one of the more pronounced effects of bromism is to the developing brain. The neurons of the human brain with their delicate bridges consisting of chemical filled synaptic gaps and concurrent ion flows that

facilitate thought processes, are dancing delicately on the tight rope wire of internal chemical balance. Multiple research studies and anecdotal reports of mental patients have confirmed that bromine interferes with normal brain functioning. The website, MedicineNet.com, Definition of Bromism (2003) describes bromism causing the symptoms of memory loss along with mental dullness, in addition ataxia, described as muscle weakness and possible slurred speech. Severe bromism can result in a temporary state that tends to mimic paranoid schizophrenia. These obvious impairments to normal functioning can also be accompanied by purplish red skin eruptions called bromoderma. The body is attempting to rid itself of the excess bromine and will deposit it within the sub dermal layers of the integument causing these eruptions.

Currently millions of metric tons of bromine salts and compounds are used world wide in a variety of industrial and agricultural applications. Any of these anthropogenic endeavors could have contributed to the finding of peaks of bromine found within samples within this study. This study is limited; therefore the exact compound the bromine might be contained within as the XRF technology only detects elemental toxins of interest.

While the list is extensive some of the more pronounced usages of chemicals that contain bromine and are anthropogenic in nature include the following descriptions.

The primary use of bromine compounds world wide is as a flame retardant or about 40% of the total usage based on 1997 figures. One of the multiple flame retardants reported by Bromine & derivatives, (1999-2009), was developed by the Albemarle Corp. called tetrabromobisphenol-A (TBBA) also called SAYTEX RB-100 which serves world wide as a flame retardant in plastics, electronic equipment and computer circuit boards.

The manufacture and sale of brominated flame retardant compounds is increasing as technologies of both the plastics and computer industries expand. These compounds serve to greatly lessen to incidence of fire and heat damage to these systems. The wide spread use of these brominated concoctions has a weighty price as they are not just inhibiting fires, but insidiously finding their way into the complex workings of the human body.

Massart et al. (2005) reported that brominated flame retardant compounds or polybrominated diphenyl esters (PBDEs) have been increasingly found world wide in human breast milk. These compounds were significant enough within mothers' milk that this study stated new mothers should have their breast milk analyzed. While Massart et al. (2005), emphasized that breast feeding is still considered the best option for the over all health of an infant, this along with other research has prompted some countries to ban usage of some brominated flame retardants (PBDEs). These countries include Sweden, Germany and the Netherlands over the time frame of the late 1980's to mid 1990's. A subsequent analysis of human breast milk showed levels of PBDEs were declining in European countries where these flame retardants had been banned. Published in the *Journal of Environmental Health Perspectives*, Betts, (2008) reported that the brominated fire retardant found PBDE in many house hold products such as carpet, curtains and bedding was finding its way into the microscopic house hold dust. In this airborne, form PBDEs were being inhaled at alarming rates. The article specifically mentioned that new studies were being conducted on this anthropogenic flame retardant effect on the function of the thyroid gland. In the *Journal of Environmental Health Perspectives*, Betts, 2008 reported the following:

> Researchers have known for years that house dust is a major exposure route for lead and certain pesticides. Now attention is turning to another class of dustborne chemicals—polybrominated diphenyl ether (PBDE) flame retardants. A growing body of research documents that PBDEs and other brominated flame retardants (BFRs) released from many different consumer products can accumulate in people's homes, cars, and workplaces. Moreover, certain segments of the population have extremely high concentrations of these substances in their bodies. However, hard data on the human health impact of these exposures are only just beginning to emerge, with many studies focusing on thyroid effects.

Betts (2008) continues as he explains that currently multiple researchers are exploring the possible connection between PBDE exposures and thyroid cancer. He reports that thyroid cancer is a disease that disproportionably affects women. The study further elaborates, according to Betts (2008), that the U.S. National Cancer Institute in their annual report stated thyroid cancers rates in women have increased since 1981 a time frame that roughly mirrors when PBDEs have been found by analysis to be in the household environments of many consumers.

Hooper and Jianwen (2002) in *Environmental Health Perspectives,* also reported on PBDEs found in human breast milk and discussed long term health concerns for infants. The exact mechanism by which PBDEs move from flame retardants on carpet, vinyl blinds or mattress pads to human milk is currently unknown. One hypothesis stated that the subtle continual vapors that surround these multiple and ever present plastic items contain PBDEs and are subsequently inhaled by residences within the home in the form of riders on microscopically tiny dust particles.

Some researchers, such as Doucet et al. (2009) over an eight year longitudinal study have noted that while the long range effect on infants have been inconclusive at this time, research on fetal tissues have shown PBDE concentrations in extracted liver

samples along with placental tissues suggest tissue specific bioaccumulation even before birth at detectable levels.

In the online journal *Science Daily*, Chemicals Used as Fire Retardants Could Be Harmful, Researchers Say, (2007), it was reported that PBDEs polybrominated diphenyl ethers have been shown in animal tests to disrupt thyroid function and be a toxin to the liver. While research studies on lab animals are profound they are also difficult and unpredictable in their subsequent extrapolation to humans. However, a specific and urgent warning was issued that many scientists worldwide are loudly pronouncing a call to err on the side of caution when it comes to the long range health of infants and young children, with whom these chemicals and their potential effects are currently little understood. Still many infants and young children receive a dose of bromine enhanced chemicals from their plastic lined mattress, toys, and clothing articles, and it would seem some manufactured food items analyzed in this study along with their own mother's milk.

The journal *Science Daily*, in the article titled, Chemicals Used as Fire Retardants Could Be Harmful, Researchers Say, (2007), it was reported that the pathway by which these brominated compounds enters the body is not fully understood, but added that one possible pathway for this to occur was within food. Additionally they discuss exposures to manufactured furniture, or carpet, which have PBDEs added at their factory of origin to inhibit a house fire spreading. Also just about any plastic product containing electrical circuitry has had PBDEs added which become quite warm when in use.

Another respected journal publication from the *American Chemical Society*, (2004) reported that when 32 food samples were analyzed the levels of concern of PBDEs were found in all the foods tested that containing animal fats. The conclusion

reached from this study was that the PBDEs tend to bioaccumulate in soluble fats. This they stated would be true for all mammals. This report studied meats from multiple markets in Dallas, Texas for contaminates. The authors noted that while their findings were preliminary, a suggestion could be made that certain foods containing soluble fats are a potential pathway by which PBDEs are entering the human body.

The second most common usage of bromine compounds worldwide is oil field drilling fluids of about 22%. of the total bromine compounds used. When explorations for new sources of oil revenue are conducted a spinning diamond tipped bit pushing against rocky structures is kept cool and lubricated with brominated compounds. As explained by the Albermarle Corporation, on their website linked to Bromine & derivatives. (1999-2009) they produce several compounds specifically utilized in oil exploration. These brominated compounds' viscosity also serves to help control the pressure in this dynamic system. Brominated compounds are utilized to stabilize areas underground in the region known as the drilling pay zone and help in the transport of other chemical additives for oil exploration. These compounds have brand names such as WELLBROM® an acronym from the terms, well and bromine. The obvious danger of toxic pollution resulting from brominated compounds usage within the oil industry would be groundwater contamination. Arkansas, according to a website titled, A Few Interesting Facts about Arkansas, (2009) located near the middle of the United States, is the largest producer of bromine from the salts known as brines deposited under ground in the region.

Local industries in this state have reportedly had occurrences of ground water pollution with bromine compounds and salts. If incidences of bromine discharge are discovered, up to 95% of all brominated compounds can be removed by reverse osmosis

by water treatment facilities. This is the norm within the United States water system. It is unknown what water treatment might be occurring in countries other than the United States. As previously discussed water serves as a vital component in food manufacturing. Rural well waters are not treated in this manner however unless the individual land owner chooses to incorporate such an enhancement into their system for potable water procurement. Oil well treatments near or in the oceans could serve as potential water pollutants also. With the vastness of the oceans and the occurrence of bromine salts naturally in this medium this would be less of a concern as compared to land locked potable water supplies.

Sodium bromide salts make up approximately 10% of the usage of bromine compounds world wide. Sodium bromide has been used as a sedative and an anti seizure medication and at one time was sold over the counter as BromoSeltzer®. This compound is no longer casually sold to consumers as its use was directly linked to multiple cases of persons erroneously being committed to mental instructions. Low level use of bromine salts for seizure disorders are in current use but must be carefully monitored. This is achieved by regulated measurement of blood levels of bromine to make sure this salt does not exacerbate itself through bioaccumulation. Bromine salts have been shown through research to accumulate in fatty deposits in the body, especially the neurons coating or myelin sheath of the brain and mammilla tissues.

Bromine salts are also a common treatment for felines or canines with seizure disorders. These household pets must also have continual blood bromine levels measured by their veterinarians as toxic levels can build up over time within tissues. Another common usage for bromine salts is as a disinfectant in hot tubs and spas. While bromine

salts look very similar to sodium chloride, both occurring as a white crystalline solid, great care must be taken by the hot tub owner that small children cannot access this potentially toxic chemical and mistake it for common sodium chloride they can sprinkle on their food. It is unknown if any studies have been conducted on the effects of bromine fumes and hot tub or spa owners. Multiple anecdotal reports concerning red eyes and coughing due to fumes when bromine was used in hot tubs are posted online. However no scientific research was found on negative physiological effects of exposures in this manner.

A less common, but more worrisome usage of bromine compounds is as a pesticide sprayed on crop land; this is largely in the form of methyl bromide. While pesticides are only approximately 8% of the world wide applications of bromine compounds they have the most direct contact with food sources. The tonnages of this pesticide every year in the United States alone is approximately 21,000 tons. Methyl bromide is used as a fumigant on crops, with about 75% of this amount sprayed on crop lands to sterilize the soil from all life. The other one fourth of this total tonnage is used during the processing and storage of food stuffs. With the pesticide methyl bromide sprayed directly onto food stuffs that feed into manufacturing of edible products it would not be unreasonable to assume some residue remains. Some organic breads, crackers and grains have adjusted their ingredient labeling to include “unbrominated flour” to ensure the persnickety consumer no bromine compounds were used in the preparation of the wheat flour or methyl bromide pesticides used in the wheat fields where the cereal grain for this specific product was grown or stored.

Worldwide the use of methyl bromide is decreasing as European countries have banned or dramatically decreased to use of this toxicant based on the negative scientific evidence. Iodomethane, a very similar molecule, is a proposed substitute that according to many scientists would be a severe environmental error. According to an article published by the associated press, *Scientists win delay of pesticide's approval* (2007), iodine would replace bromine within the molecular structure of methyl bromide and this proposed alternative would be even more dangerous to the environment. The article stated that 54 scientists, with six Nobel prize winners in their ranks, voiced astonishment that such a deadly toxin could be considered as a fumigant in wide spread crop use. Environmental groups strongly suggest that one organic chemical not replace with another as there currently are too many unknowns. Chemists who have worked with iodomethane have reported iodomethane is a very toxic substance that has been shown to alter DNA and so can be classified as a mutagen.

Multiple European countries signed a United Nations protocol to reduce or ban methyl bromides as scientists have raised an alarm of its dramatic spread. Another concern raised about methyl bromine is its long term effect on destruction of the protective ozone layer of the earth. When methyl bromine is released into the atmosphere it can find its way up eventually to the upper stratosphere where is tends to react with the fragile triangles of ozone that absorb destructive ultra violet rays.

Closer to the ground, many farm labor organizations have cited the seriously harmful effects of methyl bromide on agricultural workers. Methyl bromine has been shown by research to cause damage to the nervous system, breathing problems, convulsions and in extreme exposures, death. When pregnant female farm workers are

exposed, the resulting birth defects have been directly linked to exposures from methyl bromide. The male farm workers are not exempt from this toxin invasive effect as prostate cancers showed marked increases when males have been exposed to methyl bromide. As of the early 21st century methyl bromine is still in use across the United States as the struggle between agricultural dollars and environmental stewardship and human health continues.

A more natural approach to crop protection from insect infestation could be the use of steam in the soil before planting occurs. According to *Steam as an Alternative to Methyl Bromide in Nursery Crops* (1997), steam application can be very efficient in eliminating pest species of insects found in soils. This report stated that nursery crops comprise approximately 20% of the world's use of methyl bromide as pesticides. With the use of steam no toxic residue remains in the soil or any potential for toxic residue uptake into crop species. Currently the wide spread technology does not exist for large row crops to utilize this venue. However it could be incorporated into multiple small scale nurseries. Most small scale nurseries employ boilers for heat and these can be adapted to produce steam and then inject it in multiple directed jets through the soils to be planted. More research world wide needs to be conducted on the future large scale use of this natural and non toxic method of controlling pests that simultaneously ensures human health.

The last of a long list of other less pronounced uses of bromine compounds were as photographic fixative which is declining as digital computerized photographs increase world wide. Some photographers might still utilize a dark room with brominated

compounds fixing the images. Additionally bromine is used as an additive to rubber in the manufacturing of tires in a factory setting.

Another use of bromine is in the unlikely anthropogenic concoction, brominated vegetable oil. This strange substance was specifically created to allow miscibility of citric juices with carbonated water in beverages and inhibit undesirable layering of popular soft drinks. Hidden on the label and written in chemical code on such sodas, a consumer might find (BVO) brominated vegetable oil which was created due to its density and emulsifying qualities. The unsuspecting consumer then ingests even more bromine in their cloudy lemon lime soda. A research report by Vorhees et al., (1984), Behavioral and Reproductive effects of chronic developmental exposure to brominated vegetable oil in rats, describes how rats were fed this anthropogenic creation and the resulting effects. When the rats' diets were adjusted to contain 2% BVO this diet was found to completely block reproduction. When this was reduced to only 1% BVO for their diets, smaller litters and severely impaired growth and behavioral abnormalities were observed. This study stated that mortality was so high in this group little data could be attained for behaviors. When the BVO was further reduced to be 0.5 % of the diet, there was much less mortality observed; however behavioral impairments were equally severe as in the 1% group. Vorhees et al. (1984) concludes that the data from this study shows there is clear evidence of dose related behavioral and physical toxicity due to the ingestion of brominated vegetable oil in rats.

As previously noted extrapolating animal studies to humans is a precarious business and great caution must be taken when drawing any conclusions in this direction, currently this is the most accepted avenue for science to establish possible mammalian

harm when testing new chemicals in the environment. Since very tiny amounts of BVOs are added to popular soft drinks, it would be of value to know what percentage of a human diet yields similar results. If the consumer is a pregnant female or a small child perhaps this could be cause for concern. Currently BVOs are banned in several European countries.

Center for Science in the Public Interest (2009) reported that BVOs or brominated vegetable oils leave residues in body fats and more testing needs to be done. The site also explained that they are only used in a few products as an emulsifier, those being citrus flavored sodas that have a cloudy appearance. Therefore it is better to avoid them as this residue stored in the body's fat long term effects is largely untested at this time.

The purpose of this study was to ascertain if elemental toxins were present at significant levels in the food stuffs analyzed. Bromine was indicated to be present at significant levels in two samples manufactured in other countries. Additionally this study had a focus on only the edible products that a child six and younger including infants would be likely to consume and two non edible products that are meant to come into close oral contact, being a harmonica and a mouth harp. The form of specific compound containing the bromine atoms is beyond the scope of this study as the XRF only detects specific elemental peaks. This would be an indicator that more research should be undertaken to ascertain precisely what form the bromine detected is in. The specific form would be critical to understanding the toxic effects that might occur to the young consumers. This would be especially prudent in some cases such as the baby formula analyzed that showed a large peak of bromine. Baby formula is the powdered substitute for mother's milk and usually the only nutrition for small infants. Potentially the bromine

levels detected in this sampling might indicate a clear toxic nature to these tiny and vulnerable infants. It is largely unknown what if anything, continual exposures at such a young age might have on the developing brain and nervous system of an infant.

Some of the possible physiological effects of bromine in the human body are discussed in peer reviewed research. These focus on different organs and organ systems within the body. Research lays the foundation of understanding as to what might be occurring in medical maladies and does so with the understanding that the complex nature of the human body is still unraveling at this time.

In one study that discussed bromine and the activity of the thyroid gland, Allain et al. (1993) explains that in this research 22% of the patients that were receiving medical treatment for thyroid disorders had plasma bromine concentrations above 6 mg/L. Why this level might appear lower than the amount described as therapeutic by Ellenhorn of less than 50 mg/dL is the unit for measurement. A deciliter is equivalent to ten liters and 6 mg/L is the same as 60 mg/dL or above the 50 mg/dL established by Ellenhorn as therapeutic in nature. Another member of the halogen family, iodine is used by the thyroid gland to function correctly. Iodine is similar to bromine in many ways.

Allain et al., (1993), concludes that increases of plasma or blood level of bromine could be linked to an increase of TSH concentration assumed to be caused by iodine being replaced by bromine in this endocrine gland. Allain et al. (1996) elaborated that bromine levels were measured using inductively coupled plasma mass spectrometry in the plasma of 799 total patients all of whom had exhibited thyroid disorders. The conclusion of this study published in the *Journal of Clinical Pathology* stated that an

increase of plasma bromine could potentiate an increase in TSH levels and this was probably linked to a consequence of inhibitory effects on thyroid activity.

The thyroid is a shield shaped gland located atop the trachea inferior to the thyroid cartilage in the mid neck region. While small compared to the entire body's mass, it serves a vital function of regulating hormones directly linked to basis human functions. It must be stressed that the exact form of bromine found in samples analyzed is unknown as the delimitations of this research only allow for elemental evidence. However as research has shown a direct link to thyroid inhibition from bromine finding its way into the body, science should err on the side of caution until definitive evidence is found as to bromine compounds interference with body functions. TSH levels are part of a feed back loop from the brain where the anterior pituitary gland produces TSH (Thyroid Stimulating Hormone), this master hormone moves through the blood finding the thyroid gland where it serves as a guide for the gland to manufacture hormones. The hormones T_3 and T_4 are then released in to the blood and complete the loop back to the brain as hopefully a balance of these master chemicals is maintained. The subscripts 3 and 4 respectively refer to the numerical amount of iodine atoms in each hormone. If there is determined to be too much TSH in a person's blood they are said to suffer from hyperthyroidism, and if there is too little TSH, the medical term given is hypothyroidism. The normal range for this master hormone is reported to be between 0.4 and 0.5 mIU/L though scientists agree this amount might vary. TSH levels for infants and small children are reported to be much higher which is understandable when their accelerated growth rates are taken into account.

Bromine is more reactive than iodine and when bromine levels in the blood are high enough, Allain et al. (1996), reports that the bromine is mistaken by the thyroid as iodine, a necessary trace nutrient where it binds to this master gland. The resultant TSH levels measured in the blood of those with thyroid malfunction are due to the bromine' atoms interference with the normal uptake of the TSH and subsequent lower levels of T_3 and T_4.produced. Thyroxine (T_4) and triiodthyronine (T_3) are vital to the correct function of almost every cell of the human body. They act to regulate the metabolism and effect the production of proteins. These two hormones also regulate protein, fats and carbohydrates in the diet and how cells utilize energy from each nutrient source. They also act to regulate vitamin and nutrient uptake for different systems. Low levels of these master hormones have been linked to depression and irregular body temperature.

Multiple and rigorous studies have linked abnormal levels of these hormones to mood swings or severe depressions so much so that artificial substitutes have been synthesized in pharmaceutical laboratories for therapeutic usage. While most studies openly pronounce that the complex nature of the brains feed back system is not completely understood, chemists will state that bromine is more reactive than iodine and will replace it in.

The human race has exposed itself to many brominated compounds and salts when there are more questions than answers to their interference with thyroid function. For many years bromine salts were touted as harmless and massive amounts were sold as pharmaceuticals for a variety of maladies. One of the more common usages was as a treatment for mental disorders as it was long established that bromine compounds affect the brain and its associated functions. When mental patients were withdrawn from the

treatment of bromine salts however their indicators of mental disease dissipated or disappeared all together. This is not to say that all mental illness was controlled or cured by the withdrawal of bromine salts as a treatment. The literature has established that a certain percentage of the population that had taken over the counter bromine salts indicated worsening mental behaviors and when this percent were finally admitted to mental facilities and these bromine salts eliminated their symptoms in many cases reversed them selves or resolved them back to a normal range of mental abilities. Only within the last fifty years has a slow evolution occurred, backed by research showing the detrimental effect of high levels of the element bromine. It had originally been assumed that if a substance occurred naturally, such as bromine salts in ocean water than it must be safe and even perhaps medicinal. This is a direct parallel to the use of lead, a natural metal deemed useful whose indulgence slowly poisoned many generations.

The catch phrase, “naturally occurring”, has served as a blanket statement to cloak the complex understanding of nature’s checks and balances. Arsenic naturally occurs in some regions of this planet where it can find its way into the potable water supply and poison clusters of people, naturally of course. Of special note with the small body mass ratio to toxins is a young child and infant. This would be more of a concern possible alert to poisoning effects.

This research focused solely on edible manufactured items intended for consumption or close oral contact by children six and under and. This particular segment of the population is the sub group most at risk for poisoning effects if elemental toxins were found in these sample items.

As reported by research some bromine residues bioaccumulate in human fatty tissues and may be in our homes in our carpet and furniture as flame retardants; these leach out and float in our household dust where they are inhaled. Bromine laced flame retardants have been detected world wide in human breast milk and brominated vegetable oil is added to popular soft drinks to stabilize them from layering. Bromine compounds are being used in the exploration for oil and have been detected in potable water supplies. Additionally organic bromine compounds have been created in laboratories and injected into soils meant to enhance crop production as they are known to be so deadly they sterilize the soil of all life. Some major crops are planted under a shroud of plastic shields to keep this toxicant in place in order that strawberries and tomatoes appear perfect on the grocer's shelf as no insect could ever live through such an assault.

Bromine salts naturally occur in ocean waters and in this primeval sink are only used by certain mollusks. The human race cleverly has found brine salts from ancient seas laced with concentrated bromine salts and enveloped our planet with a cacophony of deadly brominated compounds. Research admits many are toxic such as methyl bromide when used as a pesticide. In fact, that is the very reason we have created it, to somehow keep human food stuffs segregated from the rest of the natural world by killing all creatures that live symbiotically with us.

Scientific research has overwhelmingly repeated two conclusions to date that have being published in studies that involve bromine salts and compounds.

The first conclusion is that, as far as is known at this time, tiny amounts of brominated compounds in a full grown adult would seem to have only a calming effect or no effect at all. However if bioaccumulation in fatty tissues of the body over many years

of exposure might prove positive for breast or prostate cancers or even mental dullness, caution should be exercised with self bromination.

The second conclusion is that children, small infants or even unborn fetuses are at much greater risk for bromine poisoning and even a ten fold cautionary level should be imposed for these most fragile emissaries of our future. Studies have found flame retardants in fetal tissues and in mother's breast milk. The dust in the nursery is laced with brominated compounds and the baby food from the shelf contains this element, once relegated to the sea, which has been purposefully added to our modern lives.

Recommendations

No matter the care taken, there exists a time lag in the food industries, as with each newly reported finding of possible toxins, companies must adapt to and adjust procedures to ensure the safety of there products. This is facilitated in the United States by a continual adjustment of regulation and inspections by government agencies.

This vitally important work is undertaken to ensure the American public has the best quality of food available especially food intended for small children and infants. This study found that the vast majority of edible products were very safe and well within the established levels for elemental toxins of interest. However a few were not in compliance and those few are being consumed by small children and infants or placed into their mouths as in the case of the harmonica.

The more precise question then becomes exactly how the bromine that was found in multiple samples, though under the legal allowed limit, arrived to contaminate them and is this finding significant enough to do harm to the child or infant consuming the

product. Additionally if the concentration found is sufficient to do harm, what exactly is the potential harm and to what system or systems of the human body? Once this harm has been perpetrated, can it be reversed or is there irreparable damage done?

Are medical practitioners aware of the brominated compounds so prevalent in our modern society and if so will they recognize and treat victims of bromine poisoning appropriately? If not can they be made more aware of bromine poisoning? Additionally is bioaccumulation occurring hidden deep within the child's fatty tissues with no current testing be conducted waiting like a softly ticking time bomb? A test could be created and be performed and at certain stages within a young life for this potential threat within fatty tissues.

In conclusion more research should be conducted to ascertain the answers to these serious questions. This research consisted of a survey of edible food items and one item meant for close oral contact to children six and under for three elemental toxins. Of the three, one elemental toxins of interest, lead was found to be present in at least one or more sample at significant levels. Many of the possible physiological effects of toxins in the human body are discussed in peer reviewed research. These focus on different organs and organ systems within the body. Research lays the foundation of understanding as to what might be occurring in medical maladies and does so with the understanding that the complex nature of the human body is still unraveling at this time.

The form of specific compound containing the bromine atoms is beyond the scope of this study as the XRF only detects specific elemental peaks. To follow up from this initial survey much larger samples from the identified populations of interest should be gathered which include the identified sub groups of finger foods for toddlers, fruit snacks

imported from Latin America and harmonicas imported from countries other the United States. Additionally any of the specific edible items that tested positive for high levels of lead could be reanalyzed with a larger sampling of the population of newly identified interest. Of particular interest would also be the sample of infant formula that was shown to contain high levels for bromine content, though within legal limits and is the only nutrition tiny infants consume. This was, as indicated, a survey and only one small sample of infant formula was analyzed from one container. Additionally with a much larger sample of fruit snacks from Latin America potential toxins could be found at detrimental levels. Another area of interest might be the chicken soup concentrate analyzed from Guatemala representing countries other than the United States and the United States that both were found to have very high levels of bromine. With a much large representation of the specific population in question XRF analysis could be conducted on any of these sub groups in future studies.

Another technology called (XPS) X-ray Photoelectron Spectroscopy which also uses high energy X rays could be employed if significant levels of elemental toxin were found. This technology can identify the specific number of valence electrons within a sample and obtain a reliable estimate of the specific form an elemental toxin might be in. This would be an indicator that more research should be undertaken to ascertain precisely what form the bromine that has been detected is in. The specific form would be critical to understanding the toxic effects that might occur to the young consumers. This would be especially prudent in some cases such as the baby formula analyzed that showed a large peak of bromine. Potentially the bromine levels detected in this sampling might indicate a clear toxic nature to these tiny and vulnerable consumers. The 9 samples that indicated at

a 95% confidence level for lead content above United States standards should receive priority in a larger study to better represent the population of interest. It is largely unknown what long-range effects high levels of brominated compounds or salts might have on small children's and infants developing organ systems and brain. It is well documented and accepted world wide the extremely detrimental effects lead has on the developing child. Many samples from reputable companies were shown to have extremely high standards and ROI counts for toxins far below a blank containing only distilled water. With a call to err with a ten fold concern when considering this unique sub group, better quality controls must be enforced to require all manufactures to exhibit extreme rigor of standards for toxin levels both domestic or imported.

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APPENDIXES

APPENDIX A

TABLE OF MANUFACTURED PRODUCTS

No and description	Volume	Country of origin	Purchased	$	Coin toss	Recipt	container	
US 1 animal cookies	10.0 oz	**USA**	Ks	1.99	T	2	Red box	
OC 1 animal cookies	500 g.	**Mexico**	Ok	1.00	H	1	Clear bag	
US 2 gummy children's vitamins	70	**USA**	Ks	5.49	T	6	Bottle with art	
OC 2 Gummy children's vitamins	60	**Germany**	Ks	6.36	H	6	Bottle with art	
US 3 Teddy bear cookies	10 oz	**USA**	Ks	2.04	H	2	Art on bag	
OC 3 Christmas cookies	12 oz	**Mexico**	Ok	1.00	T	1	Art on box	
US 4 Pink marshmallows	10 oz	**USA**	Ks	.88	T	4	Bag with art	
OC 4 Pink marshmallows	14 oz	**Mexico**	Ks	2.45	H	3	Bag with art	
US 5 Small biscuits	5 oz	**USA**	Ks	1.98	H	7	Yellow box	
OC 5 Small biscuits	4.2 oz	**Israel**	Ks	.63	H	5	Clear bag	
US 6 Apple juice	4 oz	**USA**	Ks	1.98	H	37	Bottle with baby	
OC 6 Apple juice	32 oz	**Germany, Holland and South Africa**	Ks	1.58	T	37	Bottle with apples	
US 7 Jelly bens	1 oz	**USA**	Ks	.49	H	2	Clear bag	
OC 7 Jelly beans	11 oz	**Mexico**	Ks	1.25	T	8	Purple bag	
US 8 Spice drops	9 oz	**USA**	Ks	.99	T	2	Bag with art	
OC 8 Spice drops	16 oz	**Mexico**	Ks	2.00	T	25	Bag with art	
US 9 Gummi worms	7 oz	**USA**	Ks	1.98	T	2	Clear bag	
OC 9 Gummi worms	8.25 oz	**Mexico**	Ks	1.88	H	5	Plastic tub	

US 10 Baby oral cleanser	.7 oz	**USA**	Ks	4.35	H	7	Baby picture	
OC 10 Baby oral cleanser	4.2 oz	**Netherlands**	Ok	1.00	H	16	Art work	
US 11 Toddler finger food	1.48 oz	**USA**	Ks	1.79	T	10	Picture of food	
OC 11 Toddler finger food	1.76 oz	**China**	Ks	1.84	T	9	Picture of baby	
US 12 Cookies	1 oz	**USA**	Ok	3.00	H	11	Metal can	
OC 12 Cookies	9 oz	**Canada**	Ks	1.18	H	39	Plastic wrapper	
US 13 Animal cookies	2.1/8 oz	**USA**	Ks	.96	T	12	Box with art	
OC 13 Cookies	14.1 oz	**Canada**	Ks	2.64	T	39	Plastic wrapper	
US 14 Chocolate drink mix	8 oz	**USA**	Ks	1.99	T	13	Can with art	
OC 14 Chocolate drink mix	14.1 oz	**Brazil**	Ok	1.50	T	1	Can with art	
US 15 Pirate shaped pasta	16 oz	**USA**	Ks	1.19	H	7	Box with art	
OC 15 abc shaped pasta	7 oz	**Mexico**	Ca	2.49	T	14	Clear bag	
US 16 Marshmallows	10 oz	**USA**	Ks	.99	T	7	Clear bag	
OC 16 Animal shaped marshmallow	1.48 oz	**China**	Ks	.99	T	15	Animal shape in plastic	
US17 chocolate drink mix	8 oz	**USA**	Ks	1.77	T	2	Box with art	
OC 17 chocolate drink mix	14.1 oz	**Mexico**	Ok	2.38	T	1	Can with art	
US 18 Toddler finger food	1.48 oz	**USA**	Ky	2.19	H	17	Cylinder with art	
OC 18 Toddler finger food	4.12 oz	**Japan**	Ks	1.39	H	18	Bag with art	

US 19 Toddler finger food	1.48 oz	**USA**	Ks	1.79	H	10	Cylinder with art	
OC 19 Toddler finger food	1.76 oz	**China**	Ks	1.84	H	9	Box with baby	
US 20 Toddler finger food	1.46 oz	**USA**	Ks	1.79	H	10	Cylinder with art	
OC 20 Toddler finger food	4.4 oz	**Japan**	Ks	1.99	T	18	Bag with art	
US 21 Pasta	5.5 oz	**USA**	Ks	1.19	T	10	Box with art	
OC 21 Pasta	17.5 oz	**Italy**	Ca	2.49	H	14	Bag with art	
US 22 Bubble gum	10 pieces	**USA**	Ks	1.09	H	10	package	
OC 22 Bubble gum	2.0 oz	**Mexico**	Ks	1.00	H	19	Plastic container	
US 23 Strawberry syrup for milk	22.0 oz	**USA**	Ks	1.19	T	10	Bottle with art	
OC 23 Strawberry powder for milk	4.0 oz	**Switzer-land**	Ok	.77	H	27	Can with art	
US 24 Animal cookies	6 oz	**USA**	Ks	1.98	T	37	Bag with art	
OC 24 Cookies	8 oz	**Canada**	Ks	2.49	T	39	Plastic wrapper	
US 25 toddler fruit treats	6 oz	**USA**	Ky	2.19	T	17	Box with art	
OC 25 Toddler fruit treats	1 oz	**Peru, China Thailand and Chili**	Ks	2.18	T	5	Bag with art	
US 26 Toddler finger food	1.1 oz	**USA**	Ky	1.49	T	17	Cylinder with art	
OC 26 Toddler finger food	1.0 oz	**Israel**	Ks	.50	T	22	Shiny bag	
US 27 Gummi bears	5 oz	**USA**	Ky	1.49	T	23	Bag with bears	
OC 28 Gummi bears	1.27 oz	**Hungary**	Ok	1.39	H	27	Bag with bears	

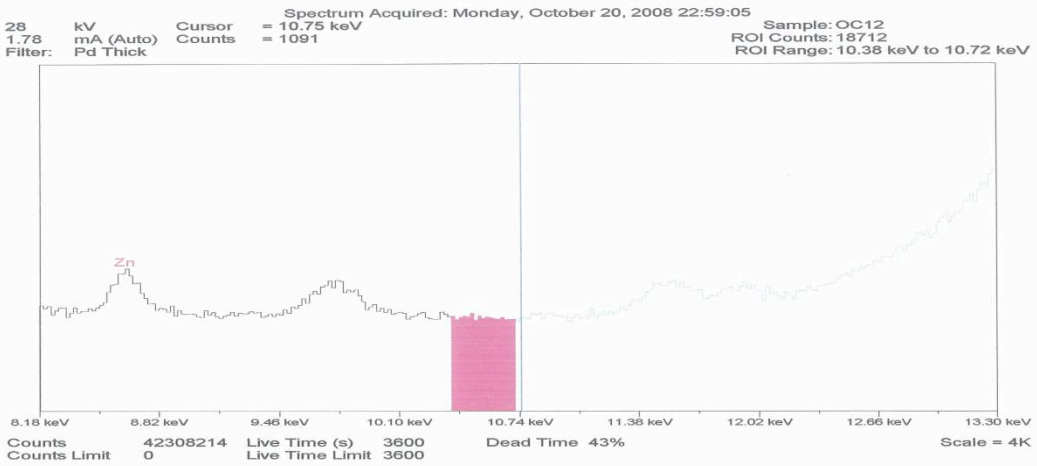
US 28 Multicolored candy	1.27 oz	**USA**	Ky	1.50	T	23	Plastic wrapper	
OC 28 Multicolored candy	3.08 oz	**China**	Ks	2.96	H	24	Hard plastic bottle	
US 29 gummi candy	7 oz	**USA**	Ky	1.49	T	17	Box with art	
OC 29 gummi candy	1.5 oz	**China**	Ok	.95	T	11	Box with art	
US 30 toy with candy	.58 oz	**USA**	Ky	1.59	T	23	Plastic toy with candy	
OC 30 toy with candy	.28 oz	**China**	Ks	2.96	H	25	Plastic toy with candy	
US 31 small finger food	6.6 oz	**USA**	Ky	1.50	T	17	Colorful wrapper	
OC 31 small finger food	5.29 oz	**France**	Ks	2.00	T	25	Colorful wrapper	
US 32 candy	4.5 oz	**USA**	Ok	1.00	H	27	Box with art	
OC 32 candy	1.7 oz	**Pakistan**	Ky	.99	T	23	Cylinder with art	
US 33 candy	8.5 oz	**USA**	Ok	1.00	H	27	Box with art	
OC 33 candy	1.41 oz	**China**	Ks	.99	H	32	Bag with art	
US 34 candy	5.25 oz	**USA**	Ok	1.50	H	27	Box with art	
OC 34 candy	.74 oz	**Spain**	Ks	1.29	T	32	Bag	
US 35 Baby formula	14.1 oz	**USA**	Ks	8.44	T	39	Cylinder with art	
OC 35 Baby formula	14.1 oz	**Mexico**	Ks	3.12	T	26	Cylinder with art	
US 36 candy	5.6 oz	**USA**	Ok	1.00	H	27	Box with art	
OC 36 candy	4 oz	**Chili**	Ok	.95	H	11	Box with art	
US 37 candy	4 oz	**USA**	Ok	.77	H	27	Box with art	
OC 37 candy	6.7 oz	**China**	Ok	2.00	H	1	Box with art	
US 38 Nursery drink	9.4 oz	**USA**	Ks	2.99	T	28	Individual bottles for infant or small child	

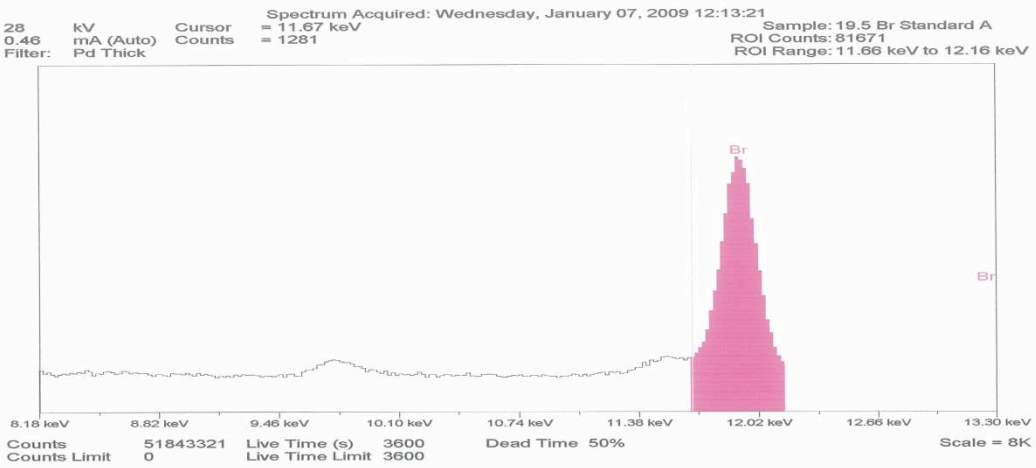
OC 38 Nursery drink	4.0 oz	**China**	Ks	4.97	H	22	Individual bottles for infant or small child	
US 39 soft cereal for small baby	8 oz	**USA**	Ks	2.98	H	37	Cylinder shaped can with lid	
OC 39 liquid drink for small baby	14.1 oz	**Mexico**	Ks	3.58	H	26	Cylinder shaped can with lid	
US 40 candy	6.00 oz	**USA**	Ok	1.00	T	27	Box with art	
OC 40 candy	1.5 oz	**Made in Canada packed in China**	Ok	1.00	T	11	Cylinder with toy	
US 41 candy	3.5 oz	**USA**	Ks	1.00	H	38	Box with art	
OC 41 candy	3.5 oz	**Mexico**	Ks	1.29	T	29	Box with art	
US 42 candy	8 oz	**USA**	Ok	1.09	T	33	Box with art	
OC 42 candy	3 oz	**Mexico**	Ks	.50	T	38	Metal can with art	
US 43 candy	12.4 oz	**USA**	Ks	1.09	H	33	Plastic bag	
OC 43 candy	.35 oz	**China**	Ks	1.49	T	30	Candy in toy phone	
US 44 candy	5.4 oz	**USA**	Ks	1.00	T	33	Shaped candy	
OC 44 candy	2.0 oz	**Spain**	Ks	.99	T	30	Colored candy	
US 45 fruit snack	5.4 oz	**USA**	Ks	1.00	H	33	Box with art	
OC 45 fruit snack	1.00 oz	**China**	Ok	1.00	T	1	Metal ball with art	
US 46 bear candy	5.4 oz	**USA**	Ks	1.00	T	33	Box with art	
OC 46 rabbit candy	40 g	**China**	Ks	1.99	T	40	Bag with art	
US 47 toddler cracker	4.0 oz	**USA**	Ks	1.72	H	34	Box with art	
OC 47 candy made into baby bottle	1.1 oz	**Thailand**	Ks	1.19	T	31	Baby bottle shaped	
US 48 oatmeal for baby	8.00 oz	**USA**	Ks	1.99	H	34	Cylinder with lid	

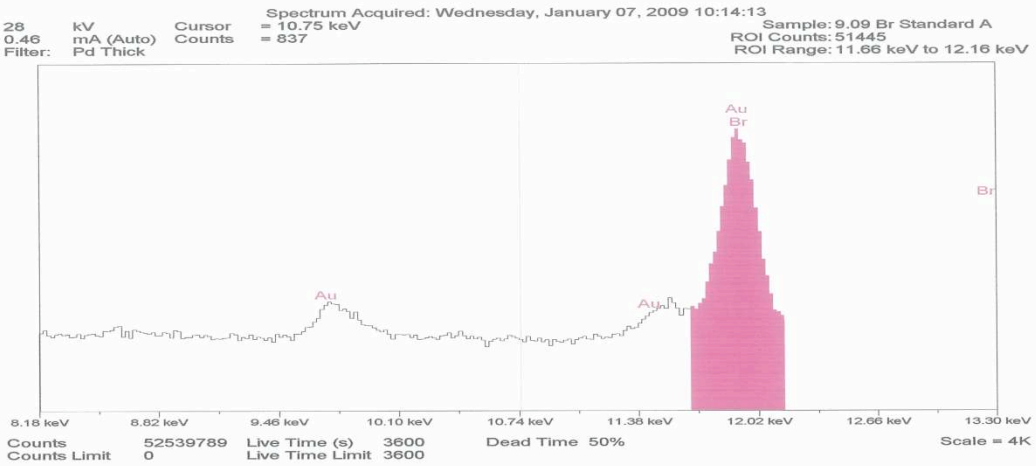
OC 48 oatmeal	16 oz	**Ireland**	Ks	5.19	H	41	Box with art	
US 49 candy	4.0 oz	**USA**	Ks	.97	H	35	Box with art	
OC 49 candy	4.5 oz	**Mexico**	Ok	1.59	T	36	Bag with art	
US 50 chicken soup concentrate	3.25 oz	**USA**	Ks	$1.59	H	35	Glass Bottle	
OC 50 Chicken soup concentrate	1 Kg	**Guatemala**	Ks	$4.98	T	39	Cylinder with art	

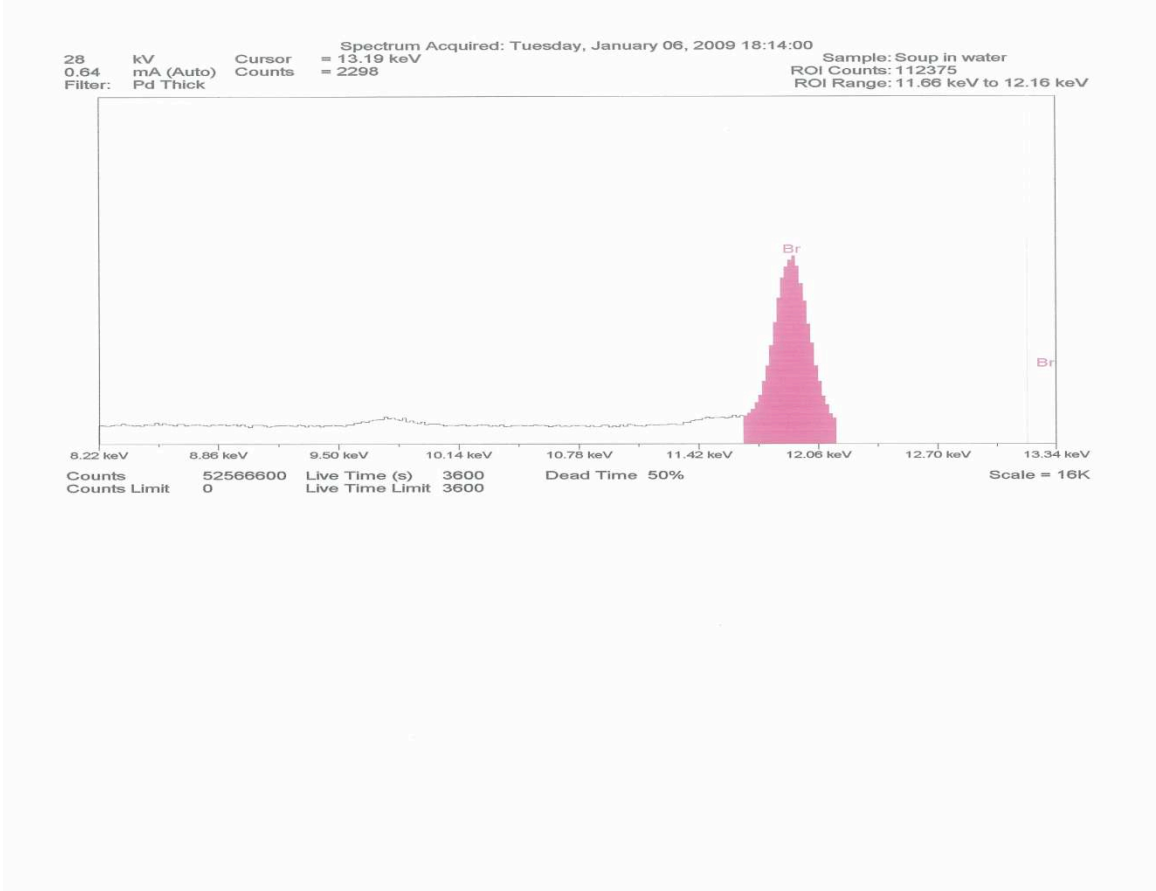
APPENDIX B

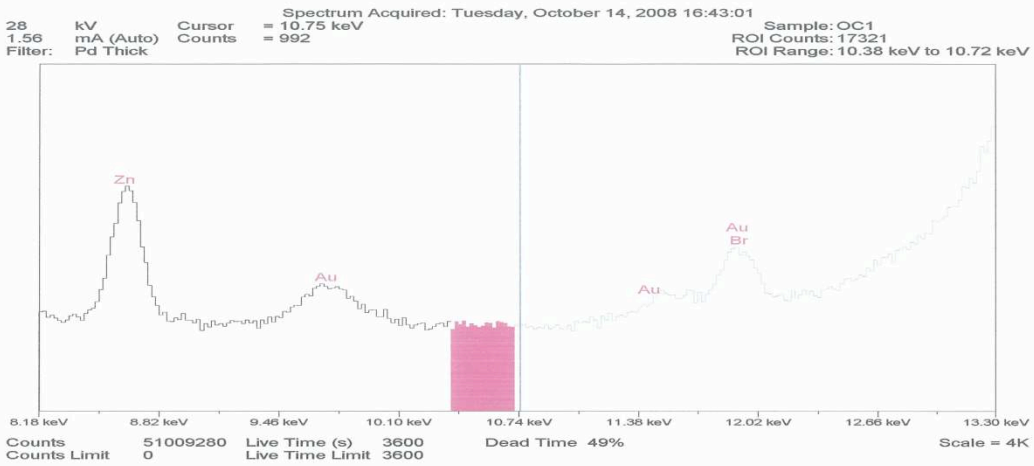
SIGNIFICANT TRIALS

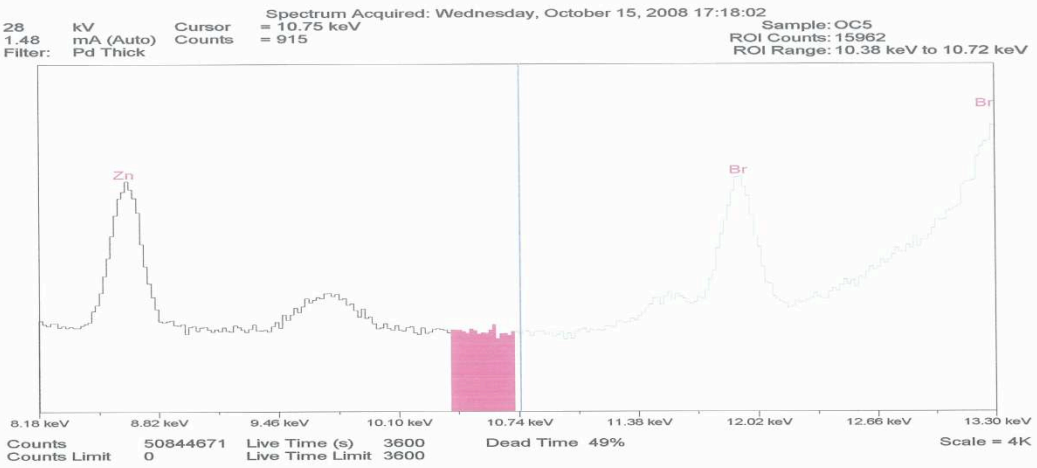

Spectrum Acquired: Monday, October 20, 2008 22:59:05
28 kV
1.78 mA (Auto)
Filter: Pd Thick
Cursor = 10.75 keV
Counts = 1091
Sample: OC12
ROI Counts: 18712
ROI Range: 10.38 keV to 10.72 keV
Zn
8.18 keV
8.82 keV
9.46 keV
10.10 keV
10.74 keV
11.38 keV
12.02 keV
12.66 keV
13.30 keV
Counts 42308214
Counts Limit 0
Live Time (s) 3600
Live Time Limit 3600
Dead Time 43%
Scale = 4K

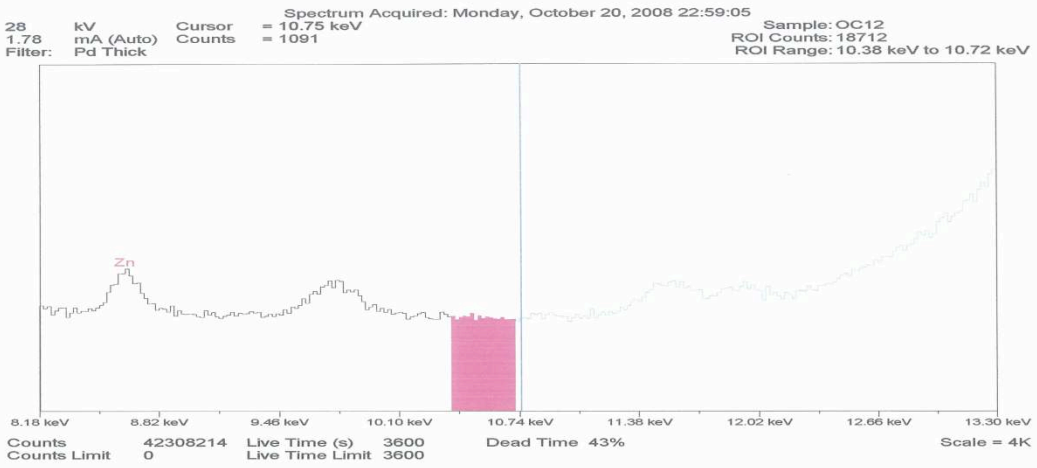

Spectrum Acquired: Wednesday, January 07, 2009 12:13:21
28 kV
0.46 mA (Auto)
Filter: Pd Thick
Cursor = 11.67 keV
Counts = 1281
Sample: 19.5 Br Standard A
ROI Counts: 81671
ROI Range: 11.66 keV to 12.16 keV
Br
Br
8.18 keV
8.82 keV
9.46 keV
10.10 keV
10.74 keV
11.38 keV
12.02 keV
12.66 keV
13.30 keV
Counts 51843321
Counts Limit 0
Live Time (s) 3600
Live Time Limit 3600
Dead Time 50%
Scale = 8K

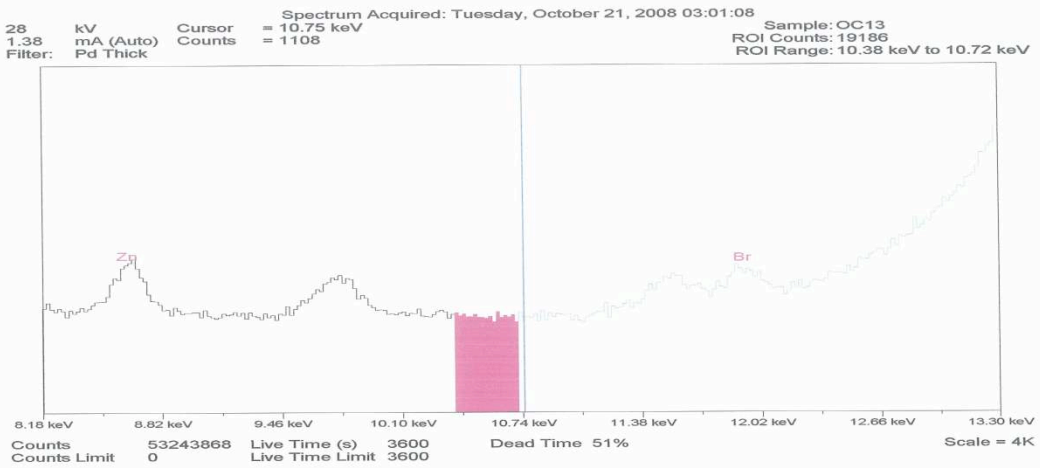

Spectrum Acquired: Wednesday, January 07, 2009 10:14:13
28 kV
0.46 mA (Auto)
Filter: Pd Thick
Cursor = 10.75 keV
Counts = 837
Sample: 9.09 Br Standard A
ROI Counts: 51445
ROI Range: 11.66 keV to 12.16 keV
Au
Br
Br
Au
Au
8.18 keV
8.82 keV
9.46 keV
10.10 keV
10.74 keV
11.38 keV
12.02 keV
12.66 keV
13.30 keV
Counts 52539789
Counts Limit 0
Live Time (s) 3600
Live Time Limit 3600
Dead Time 50%
Scale = 4K

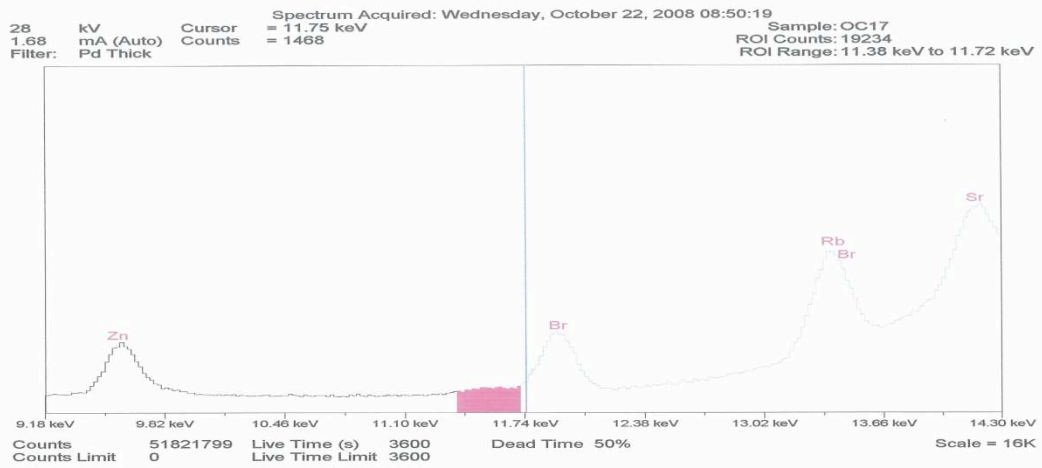

Spectrum Acquired: Tuesday, January 06, 2009 18:14:00
28 kV
0.64 mA (Auto)
Filter: Pd Thick
Cursor = 13.19 keV
Counts = 2298
Sample: Soup in water
ROI Counts: 112375
ROI Range: 11.66 keV to 12.16 keV
Br
Br
8.22 keV
8.86 keV
9.50 keV
10.14 keV
10.78 keV
11.42 keV
12.06 keV
12.70 keV
13.34 keV
Counts 52566600
Counts Limit 0
Live Time (s) 3600
Live Time Limit 3600
Dead Time 50%
Scale = 16K

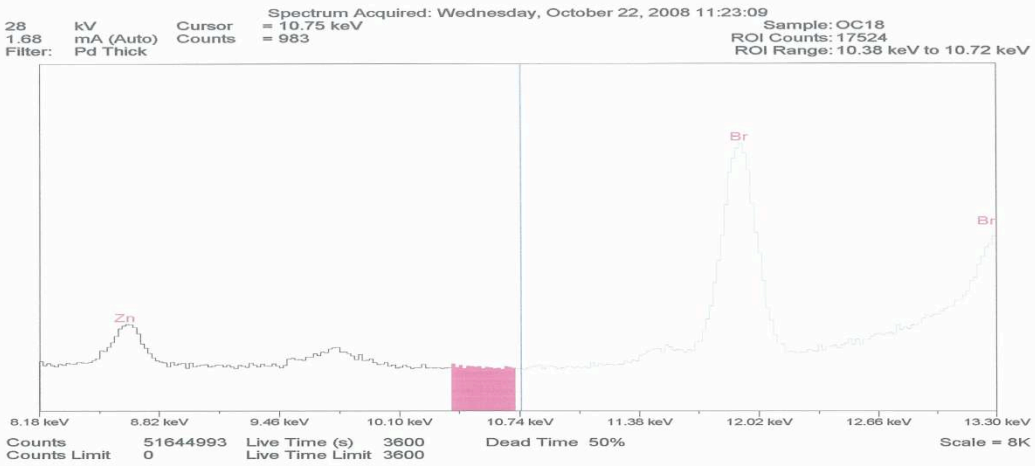

Spectrum Acquired: Tuesday, October 14, 2008 16:43:01
28 kV
1.56 mA (Auto)
Filter: Pd Thick
Cursor = 10.75 keV
Counts = 992
Sample: OC1
ROI Counts: 17321
ROI Range: 10.38 keV to 10.72 keV
Zn
Au
Au
Br
Au
8.18 keV
8.82 keV
9.46 keV
10.10 keV
10.74 keV
11.38 keV
12.02 keV
12.66 keV
13.30 keV
Counts 51009280
Counts Limit 0
Live Time (s) 3600
Live Time Limit 3600
Dead Time 49%
Scale = 4K

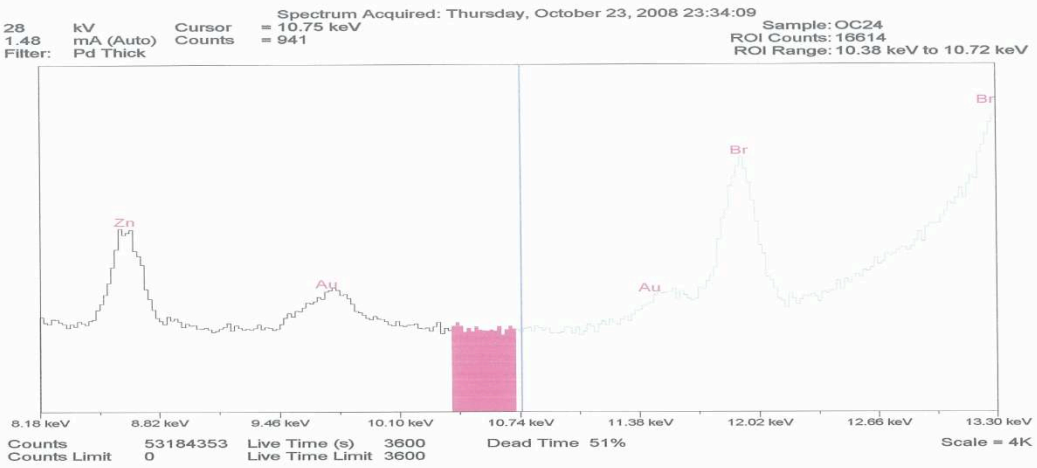

Spectrum Acquired: Wednesday, October 15, 2008 17:18:02
28 kV
1.48 mA (Auto)
Filter: Pd Thick
Cursor = 10.75 keV
Counts = 915
Sample: OC5
ROI Counts: 15962
ROI Range: 10.38 keV to 10.72 keV
Zn
Br
Br
8.18 keV
8.82 keV
9.46 keV
10.10 keV
10.74 keV
11.38 keV
12.02 keV
12.66 keV
13.30 keV
Counts 50844671
Counts Limit 0
Live Time (s) 3600
Live Time Limit 3600
Dead Time 49%
Scale = 4K


Spectrum Acquired: Monday, October 20, 2008 22:59:05
28 kV
1.78 mA (Auto)
Filter: Pd Thick
Cursor = 10.75 keV
Counts = 1091
Sample: OC12
ROI Counts: 18712
ROI Range: 10.38 keV to 10.72 keV
Zn
8.18 keV
8.82 keV
9.46 keV
10.10 keV
10.74 keV
11.38 keV
12.02 keV
12.66 keV
13.30 keV
Counts 42308214
Counts Limit 0
Live Time (s) 3600
Live Time Limit 3600
Dead Time 43%
Scale = 4K

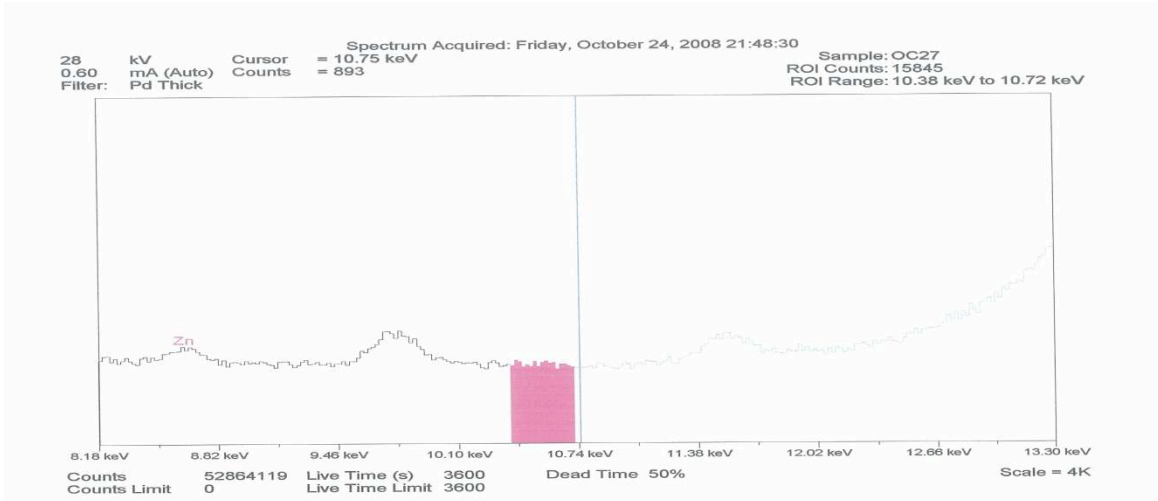

Spectrum Acquired: Tuesday, October 21, 2008 03:01:08
28 kV
1.38 mA (Auto)
Filter: Pd Thick
Cursor = 10.75 keV
Counts = 1108
Sample: OC13
ROI Counts: 19186
ROI Range: 10.38 keV to 10.72 keV
Zn
Br
8.18 keV
8.82 keV
9.46 keV
10.10 keV
10.74 keV
11.38 keV
12.02 keV
12.66 keV
13.30 keV
Counts 53243868
Counts Limit 0
Live Time (s) 3600
Live Time Limit 3600
Dead Time 51%
Scale = 4K

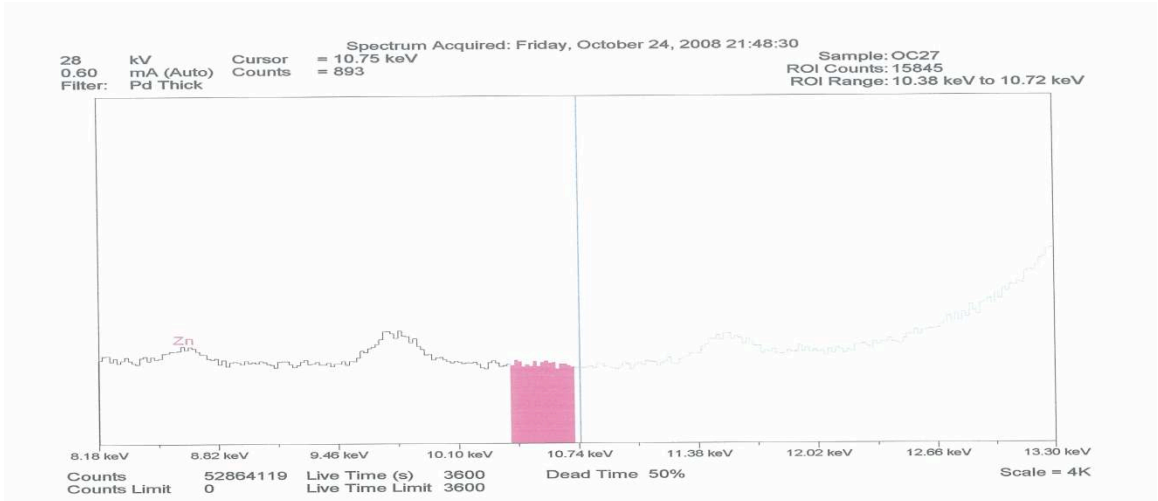

Spectrum Acquired: Wednesday, October 22, 2008 08:50:19
28 kV
1.68 mA (Auto)
Filter: Pd Thick
Cursor = 11.75 keV
Counts = 1468
Sample: OC17
ROI Counts: 19234
ROI Range: 11.38 keV to 11.72 keV
Zn
Br
Rb
Br
Sr
9.18 keV
9.82 keV
10.46 keV
11.10 keV
11.74 keV
12.38 keV
13.02 keV
13.66 keV
14.30 keV
Counts 51821799
Counts Limit 0
Live Time (s) 3600
Live Time Limit 3600
Dead Time 50%
Scale = 16K

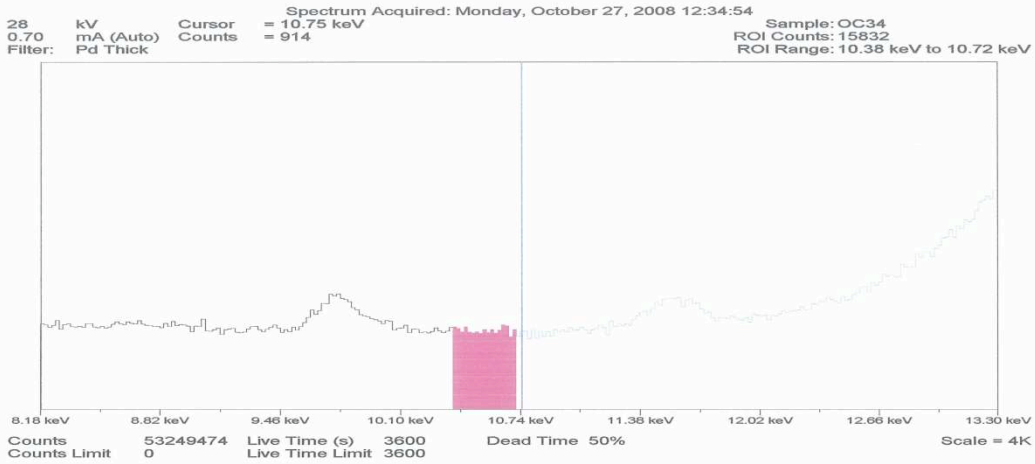

Spectrum Acquired: Wednesday, October 22, 2008 11:23:09
28 kV
1.68 mA (Auto)
Filter: Pd Thick
Cursor = 10.75 keV
Counts = 983
Sample: OC18
ROI Counts: 17524
ROI Range: 10.38 keV to 10.72 keV
Br
Br
Zn
8.18 keV
8.82 keV
9.46 keV
10.10 keV
10.74 keV
11.38 keV
12.02 keV
12.66 keV
13.30 keV
Counts 51644993
Counts Limit 0
Live Time (s) 3600
Live Time Limit 3600
Dead Time 50%
Scale = 8K

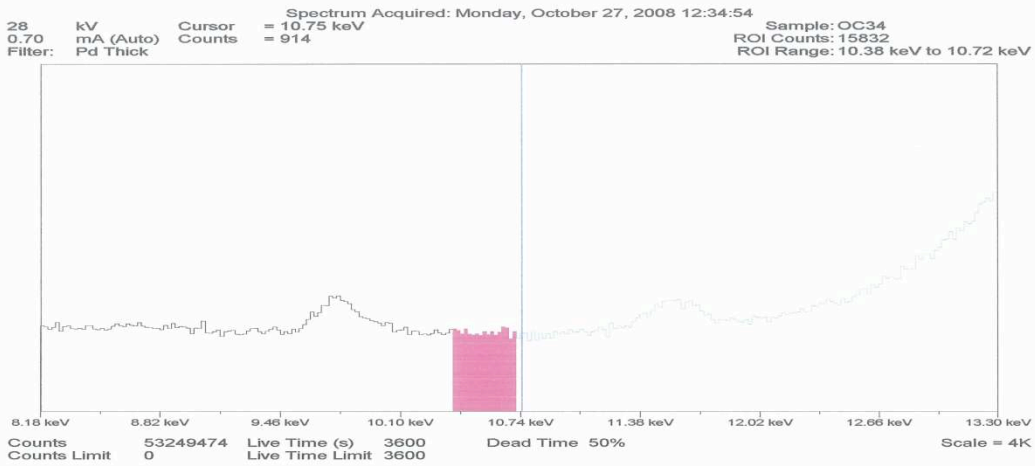

Spectrum Acquired: Thursday, October 23, 2008 23:34:09
28 kV
1.48 mA (Auto)
Filter: Pd Thick
Cursor = 10.75 keV
Counts = 941
Sample: OC24
ROI Counts: 16614
ROI Range: 10.38 keV to 10.72 keV
Zn
Au
Au
Br
Br
8.18 keV
8.82 keV
9.46 keV
10.10 keV
10.74 keV
11.38 keV
12.02 keV
12.66 keV
13.30 keV
Counts 53184353
Counts Limit 0
Live Time (s) 3600
Live Time Limit 3600
Dead Time 51%
Scale = 4K

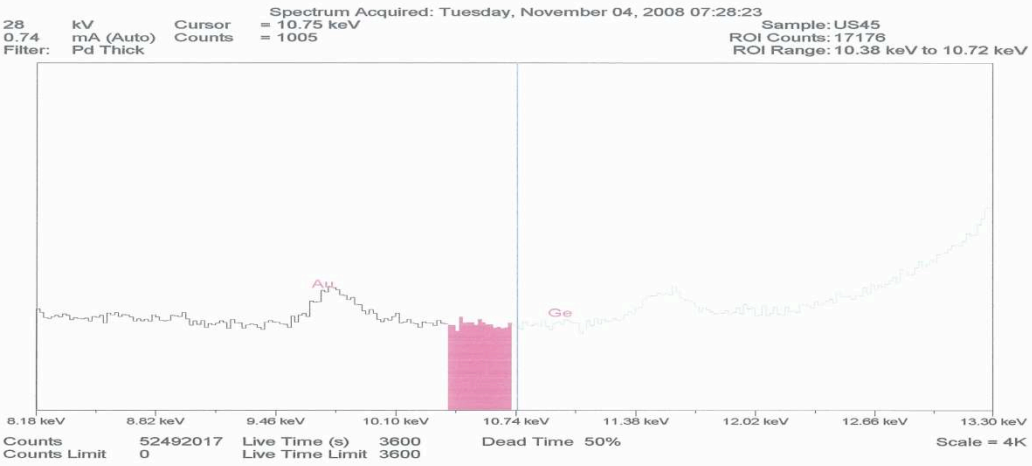

Spectrum Acquired: Friday, October 24, 2008 03:33:25
28 kV
1.56 mA (Auto)
Filter: Pd Thick
Cursor = 10.75 keV
Counts = 944
Sample: OC25
ROI Counts: 16443
ROI Range: 10.38 keV to 10.72 keV
Zn
Br
8.18 keV
8.82 keV
9.46 keV
10.10 keV
10.74 keV
11.38 keV
12.02 keV
12.66 keV
13.30 keV
Counts 51581522
Counts Limit 0
Live Time (s) 3600
Live Time Limit 3600
Dead Time 49%
Scale = 16K

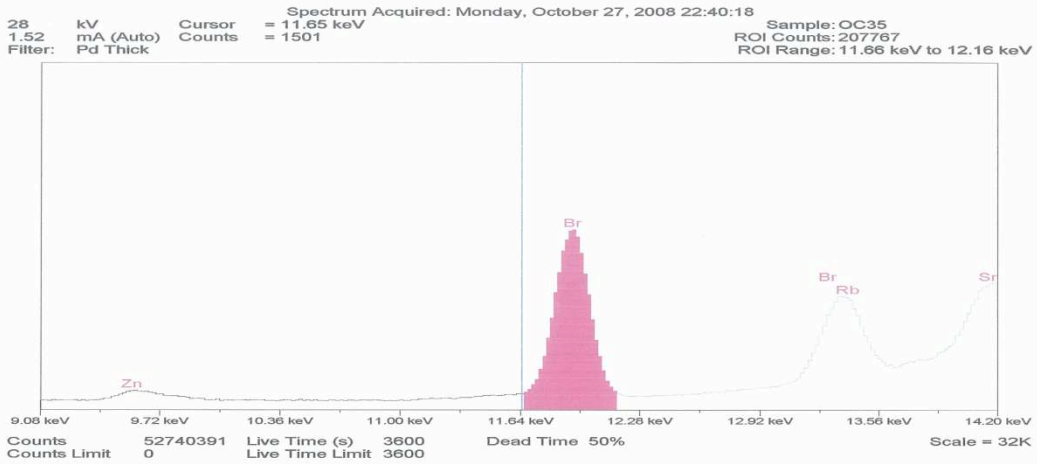

Spectrum Acquired: Friday, October 24, 2008 21:48:30
28 kV
0.60 mA (Auto)
Filter: Pd Thick
Cursor = 10.75 keV
Counts = 893
Sample: OC27
ROI Counts: 15845
ROI Range: 10.38 keV to 10.72 keV
Zn
8.18 keV
8.82 keV
9.46 keV
10.10 keV
10.74 keV
11.38 keV
12.02 keV
12.66 keV
13.30 keV
Counts 52864119
Counts Limit 0
Live Time (s) 3600
Live Time Limit 3600
Dead Time 50%
Scale = 4K

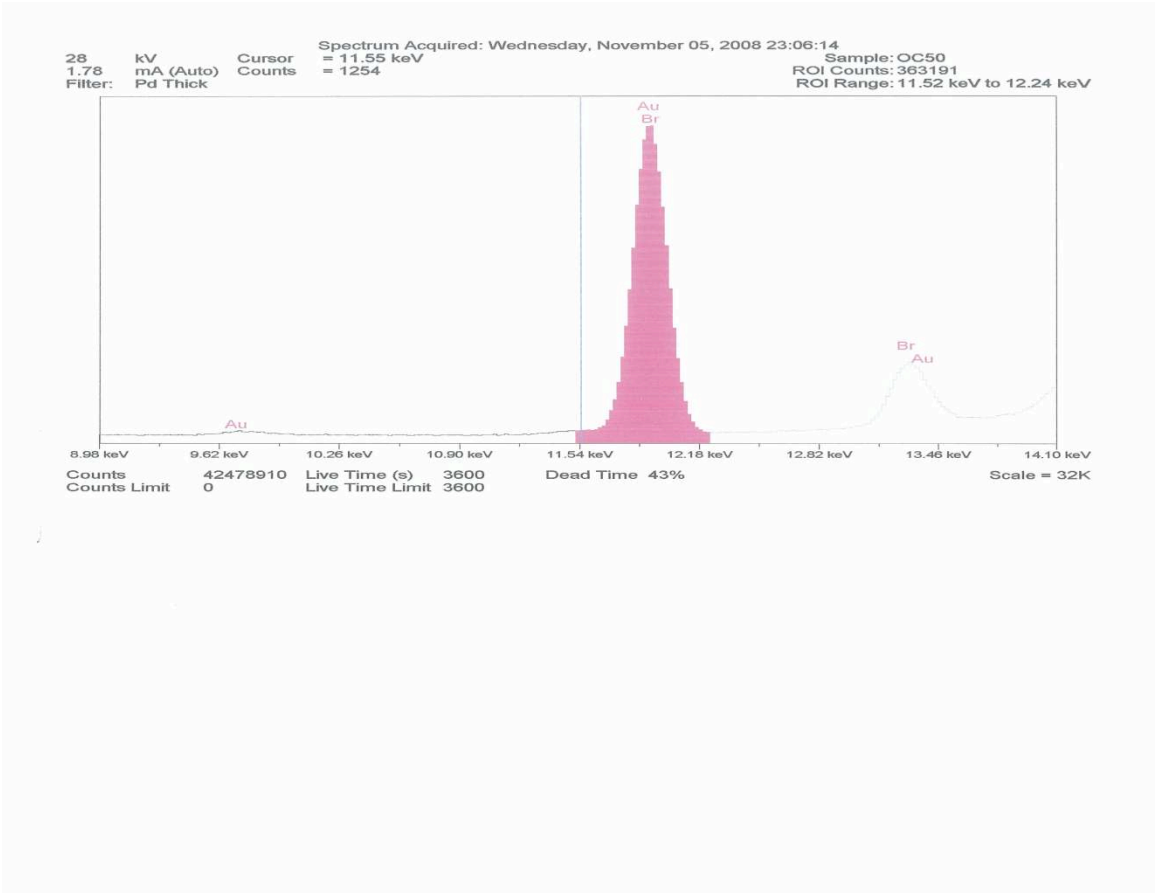

Spectrum Acquired: Friday, October 24, 2008 21:48:30
28 kV
0.60 mA (Auto)
Filter: Pd Thick
Cursor = 10.75 keV
Counts = 893
Sample: OC27
ROI Counts: 15845
ROI Range: 10.38 keV to 10.72 keV
Zn
8.18 keV
8.82 keV
9.46 keV
10.10 keV
10.74 keV
11.38 keV
12.02 keV
12.66 keV
13.30 keV
Counts 52864119
Counts Limit 0
Live Time (s) 3600
Live Time Limit 3600
Dead Time 50%
Scale = 4K

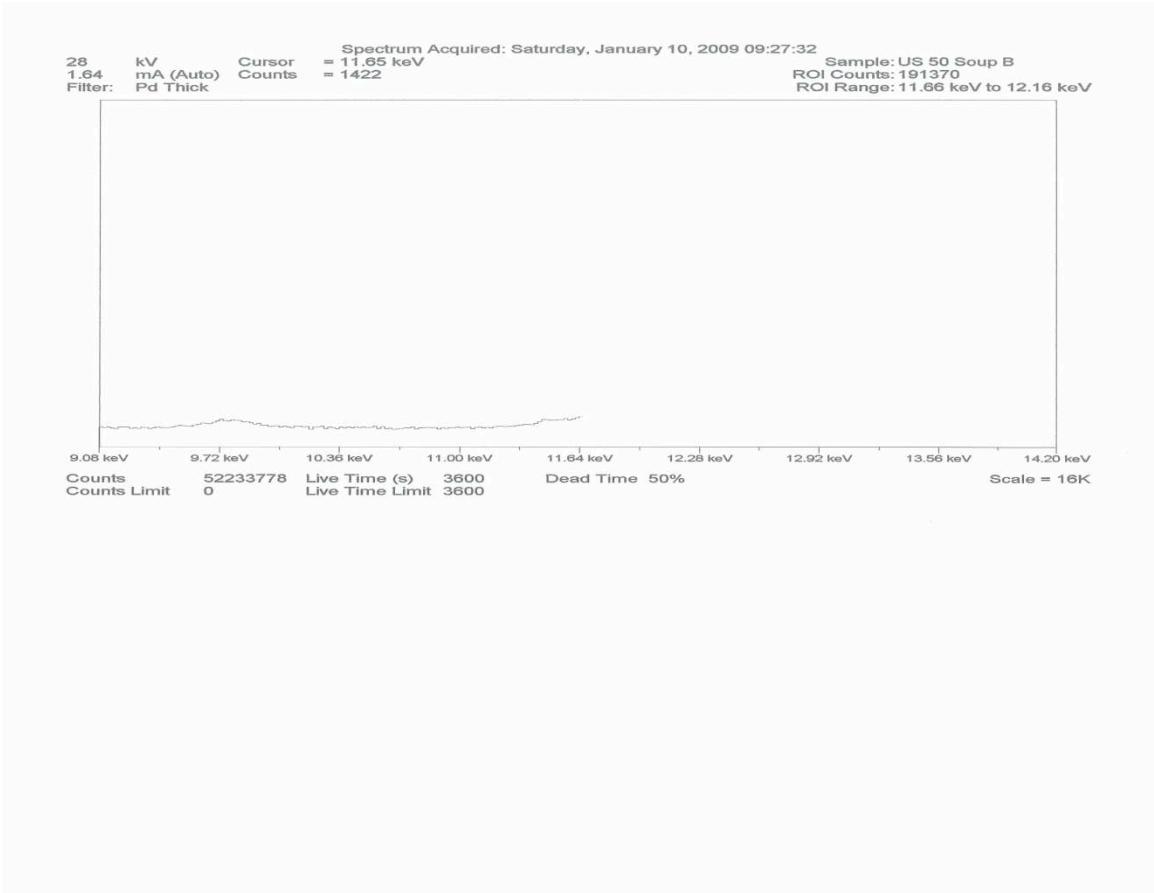

Spectrum Acquired: Monday, October 27, 2008 12:34:54
28 kV
0.70 mA (Auto)
Filter: Pd Thick
Cursor = 10.75 keV
Counts = 914
Sample: OC34
ROI Counts: 15832
ROI Range: 10.38 keV to 10.72 keV
8.18 keV
8.82 keV
9.46 keV
10.10 keV
10.74 keV
11.38 keV
12.02 keV
12.66 keV
13.30 keV
Counts 53249474
Counts Limit 0
Live Time (s) 3600
Live Time Limit 3600
Dead Time 50%
Scale = 4K


Spectrum Acquired: Monday, October 27, 2008 12:34:54
28 kV
0.70 mA (Auto)
Filter: Pd Thick
Cursor = 10.75 keV
Counts = 914
Sample: OC34
ROI Counts: 15832
ROI Range: 10.38 keV to 10.72 keV
8.18 keV
8.82 keV
9.46 keV
10.10 keV
10.74 keV
11.38 keV
12.02 keV
12.66 keV
13.30 keV
Counts 53249474
Counts Limit 0
Live Time (s) 3600
Live Time Limit 3600
Dead Time 50%
Scale = 4K


Spectrum Acquired: Tuesday, November 04, 2008 07:28:23
28 kV
0.74 mA (Auto)
Filter: Pd Thick
Cursor = 10.75 keV
Counts = 1005
Sample: US45
ROI Counts: 17176
ROI Range: 10.38 keV to 10.72 keV
Au
Ge
8.18 keV
8.82 keV
9.46 keV
10.10 keV
10.74 keV
11.38 keV
12.02 keV
12.66 keV
13.30 keV
Counts 52492017
Counts Limit 0
Live Time (s) 3600
Live Time Limit 3600
Dead Time 50%
Scale = 4K


Spectrum Acquired: Monday, October 27, 2008 22:40:18
28 kV Cursor = 11.65 keV
1.52 mA (Auto) Counts = 1501
Filter: Pd Thick
Sample: OC35
ROI Counts: 207767
ROI Range: 11.66 keV to 12.16 keV
Br
Br
Rb
Sr
Zn
9.08 keV
9.72 keV
10.36 keV
11.00 keV
11.64 keV
12.28 keV
12.92 keV
13.56 keV
14.20 keV
Counts 52740391 Live Time (s) 3600 Dead Time 50% Scale = 32K
Counts Limit 0 Live Time Limit 3600


Spectrum Acquired: Wednesday, November 05, 2008 23:06:14
28 kV
1.78 mA (Auto)
Filter: Pd Thick
Cursor = 11.55 keV
Counts = 1254
Sample: OC50
ROI Counts: 363191
ROI Range: 11.52 keV to 12.24 keV
Au
Br
Br
Au
Au
8.98 keV
9.62 keV
10.26 keV
10.90 keV
11.54 keV
12.18 keV
12.82 keV
13.46 keV
14.10 keV
Counts 42478910
Counts Limit 0
Live Time (s) 3600
Live Time Limit 3600
Dead Time 43%
Scale = 32K


Spectrum Acquired: Saturday, January 10, 2009 09:27:32
28 kV Cursor = 11.65 keV
1.64 mA (Auto) Counts = 1422
Filter: Pd Thick
Sample: US 50 Soup B
ROI Counts: 191370
ROI Range: 11.66 keV to 12.16 keV
9.08 keV
9.72 keV
10.36 keV
11.00 keV
11.64 keV
12.28 keV
12.92 keV
13.56 keV
14.20 keV
Counts 52233778 Live Time (s) 3600 Dead Time 50%
Counts Limit 0 Live Time Limit 3600
Scale = 16K

VITA

Jean M. Lake-Brown

Candidate for the Degree of

Doctor of Philosophy

Thesis: AN ANALYSIS WITH X-RAY FLUORESCENCE (XRF) SPECTROMETRY TO DETERMINE ELEMENTAL TOXINS IN MANUFACTURED PRODUCTS

Major Field: Environmental Science

Biographical:

Personal Data: Born in Marietta, OH, September, 10, 1954, the daughter of Ellen T. Lake who always encouraged education and Willis W. Lake *deceased* who always wanted a PhD at O.S.U. chuckled and added, " Ohio State University" and, step-daughter of Marjorie L. Lake whose encouragement never faltered, wife of Tommy "Joe" Brown, friend, advisor, and love of my life, without whose support this could not have been achieved.

Education: Attended three years of High School at St. Albans High School in St. Albans West Virginia finishing and graduated from Wichita High School Southeast, in May, 1973; received Bachelor of Arts in Education degree from The Wichita State University, Wichita, Kansas, 1991; completed requirements for the Master of Science in Education degree from The Wichita State University, Wichita, Kansas in 1997; completed requirements for the Doctor of Philosophy in Environmental science degree in May, 2009.

Professional Experience: High School instructor for eighteen years in science course work including Chemistry, Biology and AP Biology, along with Human Anatomy and Physiology. Junior College instructor at Butler County Community College teaching as an adjunct Professor in Chemistry and Biology over the span of multiple years.

Name: Jean M. Lake-Brown Date of Degree: May, 2009

Institution: Oklahoma State University Location: Stillwater, Oklahoma

Title of Study: AN ANALYSIS WITH X-RAY FLUORESCENCE (XRF) SPECTROMETRY TO DETERMINE ELEMENTAL TOXINS IN MANUFACTURED PRODUCTS

Pages in Study: 199 Candidate for the degree of Doctor of Philosophy

Major Field: Environmental Science

Scope and Method of Study: This research was a survey of manufactured products specifically intended for oral consumption or close oral contact by children six and younger, to ascertain if elemental toxins were present and in what quantity. The toxins of interest were lead; bromine and mercury all classified as xenobiotic. The purpose of this study was to compare two groups of the aforementioned products and ascertain of there was any statistical difference at .05α. Groups were comprised of samples manufactured in the United States and "best fit" samples manufactured in other countries and subsequently imported. X ray fluorescence spectrometry (XRF) was utilized to measure *bremsstrahlung* radiation and calculated as (ROI) counts.

Findings and Conclusions: A one way ANOVA of fifty one pairs of edible samples yielded no significant difference at .05α. Data were skewed prompting apportionment for further analysis. Results yielded differences in subcategories, "fruit snacks "was shown to be higher than the mean for lead content and samples originating from Latin America were shown to be higher than the mean for bromine content, both were rejected by Tukey-Kramer due to small sample size. Student's t test indicated differences were present in some sub groupings. Edible sample counts in Regions of Interest (ROI) were compared to a constructed calibration curve for lead and bromine content. A linear relationship was obtained from which the concentration of both toxins could be calculated using the number of counts from standardized allowable limits. Nine edible samples were found to be significant for lead content above allowable levels at a 95% confidence level. While bromine was detected none was significant at a .05α. No mercury was detected in any sample. Discussion of results indicates apportionment yielded small sample size; therefore further study is indicated to assess toxins with a new focus. Additionally research should include (XPS) to determine the exact bromine species present as this is beyond the scope of this study. Future study should include larger sample size to represent nine edible survey items found to be significant for lead.

ADVISER'S APPROVAL: Dr. Lowell Caneday