NOTE TO USERS

AN EVALUATION OF X-RAY FLOURESCENCE LEAD DETECTION METHODS FOR CANDY WRAPPERS

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ABSTRACT

An Evaluation of X-ray Fluorescence Lead Detection Methods For Candy Wrappers

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Currently, it is expensive and time consuming for public health entities to test candy (and other consumer products) that has entered the consumer market in the United States. The XRF, on the other hand, provides a quick, economical, and easy method to test lead levels. It has been demonstrated in a variety of studies that x-ray fluorescence (XRF) can be used for testing lead levels in paint, soil, and testing in-vivo for bone. What has not been studied is the XRF's ability to test for lead in certain consumer items such as candy. This research was designed to identify XRF candy testing techniques that provide a quick and accurate testing method for testing candy wrappers. If public health entities had access to XRF technology they could quickly determine if specific candies contain lead. To date, there has not been a protocol developed using the XRF instrument to test candy wrappers for lead. This study identifies which newly developed XRF procedures are the most effective for testing candy wrappers for lead.

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CHAPTER 1

INTRODUCTION

Lead is a useful element. From batteries to bullets to radiation shielding, lead has an innumerable amount of uses. Because it is rarely found in nature, lead must be mined with other ores, and then separated. Lead is very soft, highly malleable, ductile, a poor conductor of electricity, and very resistant to corrosion (EPA National Trends in Lead, 2006). These attributes make lead highly practical in a variety of applications. As one of the earliest metals utilized by humanity, lead has been used by humans for at least 7000 years, because it is abundant, easy to extract and easy to work with (Lansdown & Yule, 1986). Lead was known to the ancient Egyptians and Babylonians, and the Romans used it for pipes and in solder (Lansdown & Yule, 1986). Due to its long popularity and high usability, lead's spread throughout the environment was inevitable.

While usefulness of lead is well documented, its detrimental affects on human health are also well recognized. Lead toxicity was first recognized as early as 2000 BC (Lansdown & Yule, 1986). Nikander of Colophon wrote of lead-induced anemia and colic in 250 BC (Cheremisinoff, 1993). Acute lead poisoning can result in abdominal discomfort, nervous system damage, and encephalitis (CDC Protecting Workers Families, 2006). Chronic exposure is characterized by a blue line on the gums and can lead to damage to the brain, kidneys, nervous system, and red blood cells (CDC Protecting Workers Families, 2006). Even low levels can contribute to hypertension in older people

or to "silent lead poisoning" in exposed children, which affects the developing brain and leads to visual-motor problems and lowered intelligence (CDC Protecting Workers Families, 2006).

Though lead's detrimental affects on human health have been long known, until recently the use of lead has not been regulated. Due to the relative recent regulation of lead, many of lead's prior uses still pose a threat. Furthermore, though most industrialized nations now have regulations on leaded products, many less developed countries do not have any regulations or simply do not have the means to enforce them. In today's highly globalized society, many of the products can end up anywhere in the world as is the case with imported candy.

A variety of different types of imported candy have been shown to contain varying amounts of lead (FDA Supporting Document for Recommended Maximum Level for Lead in Candy , 2006). Children are the primary consumers of this candy and are also highly susceptible to the detrimental health effects of lead. Understanding factors that determine candy lead content and methods to test for lead content are important in determining the risk to those children consuming imported candy.

This study was designed to evaluate the lead content of different imported candy components and different colors of imported candy wrappers. Furthermore the study examined the best testing methods for detecting lead in imported candy wrappers.

CHAPTER 2

LITERATURE REVIEW

Lead is a naturally occurring element and is a member of Group 14 (IVA) of the periodic table. The atomic weight of lead is 207 (Coluccio, 1994). Lead is not a particularly abundant element, but its ore deposits are readily accessible and widely distributed throughout the world (ASTDR Toxicological Profile of Lead, 2005). The predominant lead ore is a combination of lead and sulfur called galena (Coluccio, 1994). Lead is a silver colored metal, but when it is exposed to air and water, films of lead sulfate, lead oxides, and lead carbonates are formed; these films give lead it's telltale bluish gray tone and act as a protective barrier that slows or halts corrosion of the underlying metal (Cheremisinoff, 1993). This gives lead its tell-tale bluish gray tone.

Table 1 Physical and Chemical Properties of Lead (ASTDR Toxicological Profile of Lead, 2005)

Empirical Formula	Pb
Atomic Number	82
Physical State	Solid
Color	Bluish-Gray
Atomic Weight	207.2
Melting Point, °C	327.5
Boling Point, °C	1,744
Specific Gravity	11.35

The extensive use of lead is largely due to its low melting point and excellent corrosion resistance in the environment (WHO, 1977). The commercial importance of

lead is based on its ease of casting, high density, low melting point, low strength, ease of fabrication, acid resistance, electrochemical reaction with sulfuric acid, and chemical stability in air, water, and soil (ASTDR Toxicological Profile of Lead, 2005). Many of the attributes that have made lead a popular choice for a variety of commercial purposes also make lead a detrimental element to both environmental and human health. Due to the fact that lead does not biodegrade, it can accumulate within organisms and cause a variety of problems throughout the environment (Hoelkelman, 1994).

Lead may be used in the form of metal, either pure or alloyed with other metals, or as chemical compounds (WHO, 1977). Lead is used in the manufacturing of storage batteries, lead alloys used in bearings, brass and bronze and some solders; sheets and pipe for nuclear and X-ray shielding, cable covering, noise control materials; chemical resistant linings; ammunition; and pigments and lead compounds used in glass making, ceramic glazes, plastic stabilizers, caulk, and paints (ASTDR, 2005). Lead may also be found in unexpected household items such as mini blinds, zippers, painted furniture and mineral supplements (Markowitz, 2004). In 2003, the U.S. industrial consumption of lead was: 84.2%, storage batteries; 3.5%, ammunition, shot, and bullets; 2.6%, other oxides; 2.3%, casting metals; and 1.7%, sheet lead (USGS, 2006). The use of lead in tetraethyl lead in gasoline, water pipes, solder in food cans, lead shot and sinkers, and in house paints, have led to widespread exposure of the population (www.cdc.gov, 2006). Due to human and environmental health concerns, many of these uses of lead have been phased out or are in the process of being phased out (www.cdc.gov, 2006).

Exposure Route: Air

Lead in the atmosphere comes from a wide variety of natural and anthropogenic sources (Lansdown & Yule, 1986). Natural lead dusts and volcanic eruptions account for the majority of natural lead additions to the atmosphere (Harrison & Laxen, 1981). Natural lead additions to the atmosphere pale in comparison to lead released into the atmosphere due to anthropogenic activity. The greatest source of atmospheric lead pollution was the burning of leaded gasoline. In 1984, combustion of leaded gasoline was responsible for approximately 90% of all anthropogenic lead emissions (EPA National Trends in Lead, 2006). Since the reduction and eventual ban on the use of leaded gasoline, the EPA reports a 93% reduction in lead emissions to the atmosphere between 1982 and 2002 (EPA National Trends in Lead, 2006). Other anthropogenic sources of lead include mining, primary lead production, iron and steel production, industrial uses, and the burning of oil and coal for power production (Millstone, 1997). Today, industrial processes, especially metal processing, are the major sources of lead emissions to the atmosphere with the highest lead concentrations found around smelters and battery manufacturers (Millstone, 1997). It has been estimated that 78% of emissions in 2001 were from industrial processes, 12% from transportation, and 10% from fuel combustion (EPA National Trends in Lead, 2004). It should be noted that aviation gasoline and racing fuels are not regulated for lead content and can use significant quantities of lead as well.

In the air, lead is in the form of small particles. These particles of lead can be deposited very close to their initial source, or may travel up to thousands of kilometers away (EPA National Trends in Lead, 2006). The average residence time in the

atmosphere is 10 days and is largely determined by the particles size and shape (Millstone, 1997). Smaller, more aerodynamic particles tend to remain in the atmosphere longer when compared to larger, less aerodynamic particles. Other factors, such as emission source, metrological parameters, and local geography can greatly affect lead residence time in the atmosphere and travel distance (Ratcliffe, 1981). Lead is removed from the atmosphere by precipitation or gravitational settling (EPA National Trends in Lead , 2006).

Exposure Route: Water

Lead can contaminate water by leaching from soils and rocks naturally containing lead, from industrial lead by aerial fall-out or via soils, dusts, and wastes, and from lead within the distribution system for drinking water (Ratcliffe, 1981). Lead contamination of drinking water can be attributed to a number of sources within the delivery system. The age of a home or building and the type of plumbing installed will be a major factor regarding the levels of lead in drinking water (EPA National Trends in Lead, 2005). Lead-contaminated drinking water is most problematic in buildings and residences that are either very old or very new. Older properties may have leaded pipes. On the other hand, newly soldered pipes, on which leaded solder has been used, may also pose a threat. However, lead from the newly soldered pipes can leach out if it comes in to contact with acidic water (Gooch, 1993). The solubility of lead compounds in water is a function of pH, hardness, salinity, and the presence of humic material (ASTDR Toxicological Profile of Lead, 2005). Solubility is highest in soft, acidic water. Due to this, some have hypothesized that acid rain may increase the rate at which lead leaches in a water delivery system. Also, lead piping was often used for the service connections

that join residences to public water supplies (this practice ended only recently in some localities) (ASTDR Toxicological Profile of Lead, 2005). Lead concentrations are generally highest upon "first draw" of the drinking water, due to the fact that the water has been sitting in the pipes for an extended period of time (Gooch, 1993).

Of the known aquatic releases of lead, the industrial sectors with the greatest emissions of lead and lead compounds to surface water in 2002 were, in decreasing order, electrical utilities, paper, primary metals, chemicals, and metal mining (www.epa.gov 2006). Urban runoff and atmospheric deposition are other significant indirect sources of lead found in the aquatic environment (Harrison & Laxen, 1981). Another source of lead in water is from lead shot and lead sinkers (EPA National Trends in Lead, 2006). In 1991, the U.S. Fish and Wildlife Service banned the use of lead shot when hunting waterfowl, such as geese or ducks, in order to avoid releasing lead directly to surface water (EPA National Trends in Lead, 2006). In areas receiving acid rain, the acidity of drinking water may increase; this increases the corrosivity of the water, which may, in turn, result in the leaching of lead from waste water systems, particularly from older sewer systems and sewer pipes during the first flush of water through the pipes (Millstone, 1997). The wastewater can increase lead in aquatic systems where the water is released. Lead reaching surface waters is sorbed to suspended solids and sediments (Cheremisinoff, 1993). In most surface waters and ground waters, the concentration of lead is often low due to the fact that lead forms compounds with anions in the water such as hydroxides, carbonates, sulfates, and phosphates. These compounds have low water solubility and will precipitate out of the body of water (Mundell et al. 1989).

Exposure Route: Soil

Lead is transferred continuously between air, water, and soil by natural chemical and physical processes such as weathering, runoff, precipitation, dry deposition of dust, and river flow; however, soil and sediments appear to be important sinks for lead (ASTDR Toxicological Profile of Lead, 2005). For example, lead released to the air from leaded gasoline or in stack gas from smelters and power plants will settle on soil, sediment, foliage, or other surfaces (EPA National Trends in Lead, 2006). Because it is strongly adsorbed to soil, it is generally retained in the upper layers of soil and does not leach greatly into the subsoil and groundwater except under acidic conditions such as acid rain (Coluccio, 1994, EPA National Trends in Lead, 2006). The accumulation and concentration of lead in most soils is primarily a function of the rate of deposition from the atmosphere. The heaviest contamination occurs near the highway, in the case of leaded gasoline; or near the facility, in the case of a power plant or smelter (WHO, 1977). The inner city has been cited as having an elevated level of soil lead due to the use of leaded gasoline prior to 1990 and the use of leaded paint in older housing (Gooch, 1993). The current standard for soil lead concentrations in child play areas is 400 parts per million and 1200 parts per million in non-play areas (www.epa.gov, 2006).

Exposure Route: Food

Lead can generally contaminate food in two ways; either environmental contamination prior to processing or during processing and preparation for consumption (Harrison & Laxen, 1981). Environmental lead contamination involves plants or animals becoming contaminated with lead either through air, soil, or water routes. Plants and animals may bioconcentrate lead, but biomagnification is not expected (www.epa.gov,

2006). In general, the highest lead concentrations are found in aquatic and terrestrial organisms with habitats near lead mining, smelting, and refining facilities; battery recycling plants; areas affected by high automobile and truck traffic; sewage sludge and spoil disposal areas; sites where dredging has occurred; areas of heavy hunting and fishing (lead from spent shot or sinkers); and in urban and industrialized areas (ASTDR Toxicological Profile of Lead , 2005). Lead may be present on plant surfaces as a result of atmospheric deposition; its presence in internal plant tissues indicates biological uptake from the soil and leaf surfaces (ASTDR Toxicological Profile of Lead, 2005). Uptake of lead in animals may occur as a result of inhalation of contaminated air or ingestion of contaminated plants (Racliffe, 1981). Older organisms tend to contain the greatest body burdens of lead (EPA National Trends in Lead, 2006). In aquatic organisms, lead concentrations are usually highest in low trophic level organisms and algae, and lowest in upper trophic level predators (EPA National Trends in Lead, 2006). Lead in animals is generally concentrated in bone and therefore unavailable for human consumption (Millstone, 1997). Lead in plants is generally located on the surface and can be removed by washing (Gooch, 1993). While some lead can be absorbed internally through uptake by the roots, the bioavailability of lead in soil to plants is limited because of the strong adsorption of lead to soil organic matter though this can change when the pH and/or organic matter is reduced (ASTDR Toxicological Profile of Lead, 2005).

Food may also be contaminated during processing and preparation. Lead solder used to seal canned food is a major contributor to lead contamination (Lansdown & Yule, 1986). Lead can leach out of the soldered seams, especially in canned foods which are acidic (Harrison & Laxen, 1981). Ceramic dishes may contain lead in their glazes. Lead

glazed earthenware, pottery and china can all leach lead into food if food or beverages that are cooked or stored in the vessels (Ratcliffe, 1981). The amount of lead depends on type of glaze, the length of time the food remains in the vessel, and its acidity (Ratcliffe, 1981). Leaded glass has been shown to leach into wine. The degree to which lead is released from food once it is consumed can also influence a person's uptake of lead.

Many non-Western folk remedies used to treat stomach aches or other ailments may contain substantial amounts of lead. Examples of these include: Alarcon, Ghasard, Alkohl, Greta, Azarcon, Liga, Bali Goli, Pay-loo-ah, Coral, and Rueda (ASTDR Toxicological Profile of Lead). In addition, lead may be added to these folk remedies to increase their weight and sales price (Wu et. al 1996)

A recent lead contaminated food source of concern has been Mexican candy. Chili powder, a popular ingredient in Mexican candies, can become contaminated with lead when leaded soil accumulates on chili peppers (FDA Supporting Document for Recommended Maximum Level for Lead in Candy , 2006). Lead may accumulate during the growing and handling of the chili peppers in open fields where lead contaminated soil is present (FDA Supporting Document for Recommended Maximum Level for Lead in Candy , 2006). The lead may contaminate the chili powder if the peppers are not properly washed prior to drying and grinding into chili powder (FDA Supporting Document for Recommended Maximum Level for Lead in Candy , 2006). The lead introduced by the deposited soil is further concentrated by the drying of the peppers (FDA Supporting Document for Recommended Maximum Level for Lead in Candy , 2006). In addition to a washing operation prior to grinding, actions to control soil contamination of chili peppers during all stages of the product's life have been

recommended (FDA Supporting Document for Recommended Maximum Level for Lead in Candy , 2006). Furthermore, salt based Mexican candies have become a concern due to possible lead contamination. Powdered snack mix products consisting of only salt have been shown to have elevated levels of lead (FDA Supporting Document for Recommended Maximum Level for Lead in Candy , 2006). Also of concern are the packagings the candies come in. Tamarind candy products have been found to be packed in poorly made lead glazed bowls fired at low temperatures from which very high levels of lead leached into the candy (FDA Supporting Document for Recommended Maximum Level for Lead in Candy , 2006). In addition many of the wrappers contain lead as well (Jacobs, 2002). The amount, location, and propensity of the lead to leach vary greatly among wrappers (Jacobs, R.M., 2002). In addition, many of the wrappers may contain leaded paint used to print logos on the wrappers (Jacobs, 2002).

Exposure Route: Paint

Paint as a source of lead poisoning in young children has been recognized for over a century (Ratcliffe, 1981). Lead paint had been the coating of choice for residential houses as well lead primers for steel bridges, water tanks, and other steel structures (Coluccio, 1994). An estimated 3 million tons of lead is present in the paint applied to homes nationwide (Coluccio, 1994). Addition of lead to paint gives many desirable characteristics to the finished product. Lead paints adhere better, last longer, produce a bright lasting color, and reduce the growth of mildew (Coluccio, 1994).

Although the sale of residential lead-based paint was banned in the United States in 1978, flaking paint, paint chips, and weathered powdered paint, which are most commonly associated with deteriorated housing stock in urban areas, remain a major

source of lead exposure for young children residing in these houses, particularly for children afflicted with pica (the compulsive, habitual consumption of nonfood items) (ASTDR Toxicological Profile of Lead, 2005). Lead concentrations of 1–5 mg/cm^2 have been found in chips of lead-based paint (Billick and Gray 1978), suggesting that consumption of a single chip of paint would provide greater short-term exposure than any other source of lead (EPA National Trends in Lead, 2006). An estimated 40– 50% of occupied housing in the United States may contain lead-based paint on exposed surfaces (Chisolm 1986, ASTDR, 2005). Estimates are as high as 64 million homes, or 83% of privately-owned housing units built before 1980, have lead-based paint somewhere in the building (ASTDR Toxicological Profile of Lead, 2005). Approximately 12 million of these homes are occupied by families with children under the age of 7 years (ASTDR Toxicological Profile of Lead, 2005).

Damaged lead-based paint is associated with excessive dust lead levels. Conventional renovation and demolition activities can generate large volumes of lead dust particle and chips (Collucio, 1994). Lead concentrations in dust and soil samples near newly renovated housing that had previously contained lead paint may be exceedingly high (www.epa.gov, 2006). Disturbance of older structures containing lead-based paints is now a significant contributor to total lead releases (ASTDR Toxicological Profile of Lead, 2005). Renovation and remodeling activities that disturb lead-based paints in homes can produce significant amounts of lead dust, which can be inhaled or ingested (CDC Protecting Workers Families, 2006). Exposure occurs not only through the direct ingestion of flaking and chalking paint, but also through the inhalation of dust and soil contaminated with paint (Brody et al. 1994, ASTDR, 2005).

Other Exposure Routes

Use of lead ammunition may result in exposure to lead dust generated during gun or rifle discharge (www.epa.gov, 2006), from lead pellets ingested by or imbedded in animals that are used as food sources, and from lead pellets or fragments imbedded in humans from shooting incidents (ASTDR Toxicological Profile of Lead, 2005). Exposures to airborne lead dust from firearm discharge in indoor shooting ranges has been shown to result in increases in blood lead concentration that are 1.5–2 times higher than pre-exposure concentrations (Gulson et al. 2002, ASTDR Toxicological Profile of Lead, 2005). In addition, wounds from retained bullets or shot gun pellets containing lead may be associated with lead poisoning (Lansdown &Yule, 1986). Lead may leach from the bullet, especially if the bullet is surrounded by synovial fluid (Lansdown &Yule, 1986).

A lead poisoning hazard for young children exists in imported vinyl miniblinds that have had lead added to stabilize the plastic. Over time, the plastic deteriorates to produce lead dust that can be ingested when the blinds are touched by children who then put their hands in their mouths (Norman, et al. 1997). The U.S. Consumer Product Safety Commission has requested that manufacturers change the manufacturing process to eliminate the lead (ASTDR Toxicological Profile of Lead, 2006). As a consequence, vinyl mini-blinds should now be lead-free. It has been recommended that consumers with young children remove old vinyl mini-blinds from their homes and replace them with new mini-blinds made without added lead or with alternative window coverings.

Metallic lead is another source of exposure. Lead has been used to add weight to such items as weights for fishing lines or mini blinds. In addition lead has been added to

metallic jewelry items specifically intended for children and teenagers. These items have been shown to contain varying levels of lead (Maas et al. 2005). Lead may be used to increase their weight or to impart some type of metallic coating to the surface of the item (Maas et al. 2005). In addition, toys from other countries as well as antique toys represent another area of concern for lead exposure (ASTDR Toxicological Profile of Lead, 2005). These toys may contain lead paint or may actually be made from lead.

Due to leads lustrous black appearance, it has been a popular addition to many cosmetics (CDC Protecting Workers Families, 2006). It has been especially popular for hair dyes due to hair's ability to readily absorb lead (CDC Protecting Workers Families, 2006). Some printing inks may also contain lead salts (Coluccio, 1994). These inks may be used in newspapers, magazines, or on wrappers of food products. Smoking cigarettes is another source of lead exposure.

X-Ray Florescence as a Detection Method

By far the most common lead survey testing instrument for paint is the field-portable XRF. To take a measurement, the instrument is held against a surface, then a shutter is opened using a trigger to expose the surface to the source (Harrison & Laxen, 1981). The XRF uses radioactive source (gamma emitter) to ionized lead atoms (Coluccio, 1994). Most PXRF instruments used to detect lead in materials function by bombarding the materials with X-rays emitted by radioactive cobalt (Co^{57}) or cadmium (Cd^{109}) (Coluccio, 1994). As long as the shutter is open, X-rays from the source bombard the specimen and excite atomic electrons (Cheremisinoff, 1993). A material is said to fluoresce if it emits radiation as the result of absorbing higher energy radiation from some remote source (Cheremisinoff, 1993; Gooch, 1993). As the electrons return to their ground state, X-rays

produced by the excited atoms, as well as some scattered X-rays, come into contact with the detector and are analyzed to measure lead concentration (Coluccio, 1994). Each element has a characteristic X-ray fluorescence spectrum that is independent of the composition of the material. Essentially the characteristic lead X-ray fluorescence spectrum is the same for red lead pigments as for white lead pigments (Cheremisinoff, 1993).

Most X-rays have sufficient energy to excite lead k-shell electrons to penetrate many layers (Coluccio, 1994). The X-rays produced as a result of exciting k-shell electrons also have sufficient energy so that they are not readily attenuated by atoms of other elements found in the material (ASTDR, 2005). Measurements where k-shell electrons are excited are rather sensitive to the depth of which lead atoms are present (Cheremisinoff, 1993; Coluccio, 1994). Most XRFs have settings that account for depth of the material being measured (Cheremisinoff, 1993).

Generally there are two types of commercially available instruments for measuring lead that are based on exciting k-shell electrons: lead specific and spectrum analyzer devices (Cheremisinoff, 1993). The lead-specific devices check only for lead, while the spectrum analyzer device can be programmed to analyze for other elements as well.

Toxicokinetics: Absorption

Inhalation is the major route for occupational lead exposure. Intake of lead into the body via inhalation is dependent upon the daily respired volume and the lead concentration in the inhaled air (WHO, 2006). Absorption through alveoli can vary between 10-60% for .01-μm (ASTDR, 2005). This rate is determined by factors such as particle size and ventilation rate (Cheremisinoff, 1993). Virtually all of the lead particles

that are deposited in the lower respiratory tract will be rapidly absorbed into the body (Harrison & Laxen, 1981). Larger size lead particles that accumulate in the upper nasal passageways will be carried up the airway on mucous and either swallowed or expectorated (Millstone, 1997).

Ingestion is the major route for childhood lead exposure (www.cdc.gov, 2006). Once ingested the amount of lead absorbed actually varies. About 50 percent of the lead ingested by children moves directly into the circulating blood, where it moves from organ to organ; for adults the absorption rate drop to around 10 percent (ASTDR, 2005). Non-absorbed lead will eventually be eliminated via the gastrointestinal tract through feces (WHO, 1977). Factors that affect the gastrointestinal absorption of lead include the form of lead ingested, acidity, biochemical status, and nutritional factors (Ratcliffe, 1981). For example, milk and vitamin D have been shown to increase lead absorption while calcium, iron and zinc may compete with lead absorption (ASTDR, 2005). In addition, like inhalation, smaller sized lead particles are absorbed faster and more efficiently (Millstone, 1997). Lead absorption is believed to primarily occur in duodenum, but the mechanism of action is still unknown (ASTDR, 2005).

Dermal absorption of inorganic lead compounds is generally considered to be much less than absorption by inhalation or oral routes of exposure (Cheremisinoff, 1993). However, a few studies have investigated the dermal absorption of inorganic lead in humans, and the significance of the dermal absorption pathway as a contributor to lead body burden remains uncertain (ASTDR, 2005). Relative to inorganic lead and organic lead salts, tetraalkyl lead compounds have been shown to be rapidly and extensively absorbed through the skin (ASTDR, 2005). Evidence of high dermal permeability of

organic lead compounds compared to inorganic organic salts of lead also comes from studies conducted with excised skin (ASTDR, 2005).

Toxicokinetics Distribution & Retention

Lead appears to be distributed in essentially the same manner regardless of the route of absorption. In addition, the distribution of lead appears to be similar in children and adults, although a larger fraction of the lead body burden of adults resides in bone (WHO, 2006). Lead absorbed into the body enters the bloodstream initially through plasma, and rapidly attaches itself to the red blood cells (Landsdown & Yule, 1986). Most (99%) of lead found in the blood stream is found in the red blood cell (Landsdown & Yule, 1986). There is a further rapid redistribution of the lead between blood, extra cellular fluid and other storage sites such that only about half of the freshly absorbed lead is found in the blood after a few minutes (Coluccio, 1994). The blood is distributed into tissues with the main targets being the liver, brain, and kidneys. However, about 90-95 percent of an adult's body burden (total amount of lead in blood, soft tissue, and bone) of lead is stored in the bones; for children the figure is about 70 percent (ASTDR, 2005). Many conditions can rapidly release stored lead in the bones into the blood, including pregnancy, nursing, menopause, puberty, osteoporosis, and even a fracture of the bone (ASTDR, 2005). Bones are considered long-term reservoirs of lead and can be the source of lead poisoning many years in the future (Millstone, 1997). Smaller amounts of lead are also stored in the teeth and in soft tissues such as the kidney, liver, and parts of the brain (Coluccio, 1994).

Toxicokinetics: Excretion

The half-life of lead in blood is approximately 36 days for adults, while the half life for a 2 year old child may be as long as 10 months (Coluccio, 1994; ASTDR, 2005). Lead stored in bones in both children and adults generally has a half life of 25 years and about 40 days for soft tissue (Coluccio, 1994; ASTDR, 2005). Stored lead is excreted from the body by the kidneys at a very slow and steady rate and smaller amounts of lead are eliminated through the gastrointestinal tract via the bile duct (ASTDR, 2005). Because of this slow elimination process, individuals who are removed from lead contaminated environments due to high blood lead levels may not achieve normal levels for months, and sometimes years (Coluccio, 1994; Cheremisinoff, 1993).

Toxicokinetics: Biomarkers of Lead Exposure

The ideal biomarker of lead exposure would be a measurement of total lead body burden. Biomarkers of exposure in practical use today are measurements of total lead levels in tissues or body fluids, such as blood, bone, urine, or hair; or measurement of certain biological responses to lead (WHO, 2006; ASTDR, 2005). Of these, blood lead concentration (PbB) is the most widely used and considered to be the most reliable biomarker for general clinical use and public health surveillance (Coluccio,1994) . Currently, blood lead measurement is the screening test of choice to identify children with elevated PbBs (CDC Protecting Workers Families, 2006).

In October of 1991, the Centers For Disease Control (CDC) published a document entitled Preventing Lead Poisoning in Young children, which lowered its definition of elevated blood lead levels from 25ug.dl to 10ug/dl for preschool children and established an intervention strategy based on blood lead levels (www.cdc.gov, 2006).

One of the weaknesses of measuring blood lead levels is that it only measures circulating lead levels, not the stored levels in the bones and teeth. Blood comprises <2% of the total lead burden; most of the lead burden resides in bone especially in adults (ASTDR Toxicological Profile of Lead, 2005). Blood lead level does not reveal lifetime history of exposure, but provides a "snapshot" of the most recent exposure (Millstone, 1997). The elimination half-life of lead in blood is approximately 30 days. Therefore, the lead concentration in blood mainly reflects the exposure history of the previous few months and does not necessarily reflect the larger burden and much slower elimination kinetics of lead in bone (Coluccio, 1994). In addition, blood lead levels may be influenced by lead that is released from the bone and other storage sites in the body, so that elevated blood lead levels may be measured even in the absence of recent lead exposure (WHO, 2006).

The development of noninvasive XRF techniques for measuring lead concentrations in bone has enabled the exploration of bone lead as a biomarker of lead exposure in children and in adults. Lead in bone is considered a biomarker of cumulative exposure to lead because lead accumulates in bone over the lifetime and most of the lead body burden resides in bone (Coluccio, 1994; WHO, 2006; ASTDR, 2005). Lead is not distributed uniformly in bone (WHO, 2006). Lead will accumulate in those regions of bone undergoing the most active calcification at the time of exposure (Lansdown and Yule, 1986).

Lead generally accumulates in trabecular bone during childhood, and in both cortical and trabecular bone in adulthood (ASTDR, 2005). Patella, calcaneus, and sternum XRF measurements primarily reflect lead in trabecular bone, whereas XRF measurements of

the midtibia, phalanx, or ulna reflect primarily lead in cortical bone (ASTDR, 2005). Tooth lead has been considered a potential biomarker for measuring long-term exposure to lead because lead that accumulates in tooth dentin and enamel appears to be retained until the tooth is shed or extracted (Coluccio, 1994; Lansdown and Yule, 1986; WHO, 2006). Lead measurements in teeth and bone are a better index of cumulative lead exposure and are better suited for epidemiological studies, rather than used as a basis for regulatory action involving individual cases of lead poisoning (Lansdown and Yule, 1986, Coluccio, 1994).

Health Effects: Hematological

When lead is absorbed into the bloodstream, it will attach to the erythrocytes (red blood cells) and shorten their lifespan (Coluccio, 1994). This is due to the fact that lead interferes with the enzyme ATPase, resulting in "mechanical fragility" of the cell (Lansdown & Yule, 1986; ASTDR, 2005). Lead may also interfere with the production of both hemoglobin and blood cells resulting in anemia (Coluccio, 1994). The affects of anemia are well-known and include fatigue, exhaustion, and pale coloring. Lead is also known to reduce hepatic heme, upon which enzyme formation occurs, resulting in a lowering of the body's ability to detoxify pollutants (Lansdown & Yule, 1986; WHO, 2006). This can produce a variety of health problems, which under initial examination, may appear unrelated to lead exposure. Adverse impacts on the heme formation pathway and on vitamin D and calcium metabolism, all of which have far-reaching psychobiological effects, have been documented in children with 15- 20 μg/dl blood lead levels (ASTDR, 2005, WHO, 2006). Blood lead levels of 40 μg/dl and greater have an even greater affect (ASTDR, 2005, WHO, 2006).

Health Effects: Renal

Chronic exposure to lead can eventually interfere with the ability of the kidney to filter the blood which is known as nephropathy. Kidney damage is irreversible and has been recognized as a disease affecting many lead workers. Nephrotoxicity results because the kidney is the main route of elimination of lead (Pranay, 2005). Lead is absorbed by the proximal tubular cells of the renal tubules, where it binds to specific lead-binding proteins (Pranay, 2005). The lead accumulates in the mitochondria and causes both structural and functional alterations (Pranay, 2005). The effects include mitochondrial swelling and the inhibition of respiratory function and energy (ATP) production (Coluccio, 1994). As a result, energy-dependent processes, including tubular transport, are impaired (Coluccio, 1994; Pranay, 2005). Patients with chronic lead nephropathy may have a progressive decline in kidney function and eventually require kidney replacement. Acute lead nephropathy, which is mainly seen in children, is often reversible once the exposure has been eliminated (Coluccio, 1994).

Health Effects: Neurological & Neurobehavioral

One of the more profound effects of lead poisoning is that associated with the severe damage of the central nervous system. The central nervous system is the most sensitive target of lead poisoning. At extremely high levels, lead exposure can cause brain damage resulting in encephalopathy, hallucinations, blindness, convulsions, coma, and possibly death (ASTDR, 2005; WHO, 2006; Millstone, 1997). At lower levels lead may cause malaise, forgetfulness, irritability, lethargy, headache, fatigue, impotence, decreased libido, dizziness, weakness, and paresthesia (ASTDR, 2005; WHO, 2006; Millstone, 1997). It is also widely recognized that neural damage due to lead poisoning is

irreversible (Coluccio, 1994). Low levels of lead exposure, however, have a more dramatic affect on children during their developmental stages than adults (Khan, 2004). Chronic lead exposure among children can result in low IQ scores, reading disabilities, inability to concentrate, and reduced classroom performance (ASTDR, 2005: WHO, 2006; Khan, 2004). It can also affect hand eye-hand coordination, motor skills, and hearing (ASTDR, 2005; WHO, 2006). Many of these symptoms are believed to be irreversible and are largely attributed to the incomplete development of the blood brain barrier. Lead interferes with the endothelial cells during the childhood, disrupting the development of the blood brain barrier (Kahn, 2004). In addition, lead interferes with calcium homeostasis and can replace calcium in the calcium-sodium ATP pumps, reducing energy production in the brain (Kahn, 2004).

Health Effects: Cardiovascular

Greatly elevated blood pressure has been documented as a result of a large, acute lead exposure. This is the result of extreme constriction of the blood vessels which occur at levels above 70μg/dl (WHO, 2006). Though some studies have shown a relationship between lead and increased blood pressure below 70μg/dl, the topic remains controversial. Epidemiological findings have found a persistent trend in the data that supports a relatively weak, but significant association (ASTDR, 2005). It has been estimated that persons today have blood lead levels 200-500 greater than pre-industrial man (Gooch, 1993). Some have hypothesized that these blood lead levels, which may increase blood pressure moderately, may have a profound effect on hypertension among the population as a whole (WHO, 2006).

Health Effects: Other

Lead affects the reproductive organs and activities of both men and women. Chronic lead exposure has been associated with male infertility, stillbirths, and miscarriages (Coluccio, 1994). Moderate lead exposure has been associated with low male sperm counts in addition to abnormal sperm cells and/or decreased sperm mobility (Collucio., 1994). Lead may also reduce libido in men, and in women lead exposure may manifest itself in abnormal menstrual cycles and decreased fertility (ASTDR, 2005).

Lead may also affect the gastrointestinal tract. Lead exposures that result from ingestion may cause symptoms that include constipation and acute abdominal pain called "lead colic" (Gooch, 1993). Lead may also result in diarrhea, nausea, and vomiting (WHO, 2006; Lansdown & Yule, 1986).

One of the least studied areas involving the health effects of lead is its carcinogenicity. Both the International Agency for Research on Cancer and the U.S. Environmental Protection Agency have concluded that lead is a carcinogen based on laboratory tests performed on animals (EPA National Trends in Lead, 2006; www.iarc.fr, 2006). However, both organizations have concluded that human data are inadequate to refute or confirm lead as a carcinogen in humans (EPA National Trends in Lead, 2006; www.iarc.fr, 2006). It is believed that lead increases the risk of cancer by reducing the ability of cells to protect or repair DNA damaged by other exposures, rather than altering DNA directly (ASTDR, 2005).

Populations Unusually Susceptible

A susceptible population will exhibit a different or enhanced response to lead than will most persons exposed to the same level of lead in the environment (ASTDR, 2005).

Reasons may include genetic makeup, age, health and nutritional status, and exposure to other toxic substances (Lansdown & Yule, 1986). Certain subgroups of the population may be more susceptible to the toxic effects of lead exposure. These include crawling and house-bound children (<6 years old), pregnant women (and the fetus), the elderly, smokers, alcoholics, and people with genetic diseases affecting heme synthesis, nutritional deficiencies, and neurological or kidney dysfunction (ASTDR, 2005; WHO, 2006).

Young children and fetuses are at greatest risk for lead poisoning, especially those living in urbanized, low-income housing (ASTDR, 2005; WHO, 2006). Children less than 72 months of age, particularly those less than 36 months are at an especially increased risk of lead poisoning (Collucio, 1994). This is largely due to the fact that children engage in hand-to-mouth activity which greatly increases their ingestion of lead (Markowitz, 2004). Behavior such as thumb sucking and pica result in an elevated transfer of lead-contaminated dust and dirt to the gastrointestinal tract (Markowitz, 2004). Further more, young children (<5 years old) have been documented to absorb lead via the gastrointestinal tract more efficiently (50% relative absorption) than adults (15% relative absorption) (ASTDR, 2005). For example, the diets of young children are commonly deficient in zinc, a condition that exacerbates some of the toxic effects of lead (WHO, 2006). Children have also been documented to have lower blood thresholds for the hematological and neurological effects induced by lead exposure (Landsdown and Yule, 1986). In addition, the resultant encephalopathy, central nervous system deficits, and neurological sequelae tend to be much more severe in children than adults (Collucio,

1994). Breast-fed infants of lead-exposed mothers are also a susceptible group since lead is also secreted in the breast milk (ASTDR, 2005).

The embryo and fetus are at increased risk because of transplacental transfer of maternal lead (WHO, 2006). If the mother receives excessive exposure to lead years prior to the pregnancy she may transfer lead to the fetus. Studies of women suggest that conditions of pregnancy, lactation, and osteoporosis may intensify bone demineralization, thus mobilizing bone lead into the blood resulting in increased body burdens of lead (ASTDR, 2005). Women with postmenopausal osteoporosis may be at an increased risk since lead inhibits activation of vitamin D, uptake of calcium, and several aspects of bone cell function to aggravate the course of osteoporosis (Lansdown and Yule, 1986). The aged population may be at an increased risk for toxic effects of lead associated with decreased neurobehavioral performance (ASTDR, 2005; WHO, 2006). Bone lead may chronically remobilize into blood, thus accelerating cognitive decline (ASTDR, 2005; WHO, 2006).

Methods for Reducing Toxic Effects

The best treatment for lead poisoning is prevention. The management of an individuals lead poisoning potential involves eliminating the lead source from their environment, providing general medical care with a specific focus on lead detection, educating people on the hazards of lead, and recognizing potential sources of lead contamination (Gooch, 1993).

General recommendations to reduce absorption of lead following acute exposure include removing the individual from the source of exposure and decontaminating exposed areas of the body (Cheremisinoff, 1993). Contaminated skin is washed with soap

and water, and eyes exposed to lead are thoroughly flushed with water or saline (Cheremisinoff, 1993)

Lead absorption from the gut appears to be blocked by calcium, iron, and zinc. Although no treatment modalities to reduce lead absorption have yet been developed that make use of these observations, it is recommended that a child's diet contain ample amounts of iron and calcium to reduce the likelihood of increased absorption of lead and that children eat regular meals since more lead is absorbed on an empty stomach (CDC Protecting Workers Families, 2006). Good sources of iron include liver, fortified cereal, cooked legumes, and spinach, whereas milk, yogurt, cheese, and cooked greens are good sources of calcium (CDC Protecting Workers Families, 2006).

All of the currently available methods to obviate the toxic effects of lead are based on their ability to reduce the body burden of lead by chelation (ASTDR, 2005). All of the chelating agents bind inorganic lead, enhance its excretion, and facilitate the transfer of lead from soft tissues to the circulation where it can be excreted (WHO, 2006). The success of chelation therapy depends on excretion of chelated lead via the kidney (Coluccio, 1994).

Lead content in candies, especially those from Latin America, is an important issue. Children are the primary consumers of this candy and children are also a highly susceptible population to the detrimental affects of lead. Developing proper testing methods to determine factors that may increase the likelihood of lead in imported candy is of great importance. Due to its ease of use and relative wide availability in lead detection, X-Ray Fluorescence is an excellent candidate for use in screening imported candies for lead content. Further research is needed to develop proper testing protocols

and to determine which candy and candy packaging may be at higher risk for lead contamination. This research project is intended to help determine proper testing protocols for testing imported candy as well as determining important factors which may contribute to lead contamination.

CHAPTER 3

METHODOLOGY AND DATA DESCRIPTION

Research Questions

- What XRF testing methods are most effective in determining candy and candy wrapper lead content?
- What factors affect imported candy and candy wrapper lead content?
- Can National Institutes of Health (NIST) standards be modified to test chemical lead test kits?

Objectives

- To determine the best method for using the XRF as a screening tool for candy wrappers
- To determine if wrapper attributes affect lead content.
- To assess the suitability of NIST standards for evaluating chemical lead test kits.

Hypotheses

- XRF Thin Sample Mode – 4 Quadrant & Middle will be the most accurate wrapper analysis technique.
    - A Pearson's Correlation will be used to compare XRF wrapper analysis method results with the results of Graphite Furnace Atomic Absorption Spectrometry.
        - n=35

- Imported candy wrapper lead content will be independent of wrapper color.
    - A Chi-Squared test will be used to analyze frequency of the presence of lead content by color of candy wrapper.
        - n=30
- Lead concentrations will remain the same in pre-peeled standards and post peeled standards.
    - A paired T-Test will determine lead concentration differences between pre-peeled and post-peeled lead standards.
        - n=95

Methodology

Lead content was analyzed using a Portable X-ray Fluorescence machine; model XLp 303A from Niton Corporation (Boston, MA). The instrument analyzes total lead concentration using a Cadmium source. The XRF automatically cools the detector and performs a self calibration when powered up. Quality assurance and control was performed with certified lead standard provided by Niton Corp. The XRF was calibrated prior to testing, after every 50 measurements, when switching analysis modes, and upon completion of testing. Instrument calibration was tested using standards provided by Niton Corp. Standards were tested by taking three measurements in bulk sample mode, three measurements in paint mode, and three measurements in thin sample mode using the appropriate standards provided.

A convenience sample of imported candies was collected from various locations throughout the Las Vegas Valley. At the laboratory, wrappers were removed from the candy and were placed into protective containers. Each wrapper was given a unique

identification number which was written on its container. A sample of 35 wrappers was chosen with care taken to represent low, medium, and high wrapper lead concentrations. The wrappers were analyzed using 3 different XRF modes and five different wrapper analysis methods as follows:

Table 2 XRF Modes and Wrapper Analysis Methods

Mode	Method	Wrapper Placement
Thin Sample	Single Shot	Laid flat against XRF window
Thin Sample	4 Quadrant & Middle	Laid flat against XRF window
Thin Sample	Folded Wrapper	Folded to 1 cm^2
Dust Wipe	Dust Wipe	Folded to fit dust wipe holder
Bulk Cup Mode	Soil	Crumpled into soil cup

Thin Sample Mode

The XRF was set to thin sample mode with an analysis time of 30 seconds then placed in a protective holding stand provided by Niton Corp. *Single Shot Method*: The wrapper was removed from its protective container and laid flat across the XRF analysis window with the center of the wrapper over the center of the XRF analysis window. An effort was made to keep the wrapper as flat as possible with minimal space between the XRF and the wrapper. The wrapper was then analyzed and the results were recorded. The method was repeated for all 35 wrappers.

4 Quadrant + Middle Method (Figure 3- 1*)*: The wrapper was removed from its protective container and laid flat across the XRF analysis window. The wrapper was divided into 4 quadrants as well as a 5th location in center of the wrapper where the four quadrants intersect (*Figure 3-1*). An effort was made to lay the wrapper as flat as possible with minimal space between the XRF and the wrapper. Starting with quadrant A, the wrapper was then analyzed in the center of each of the five quadrants and the results were recorded. The method was repeated for all 35 wrappers.

Folded Wrapper Method: The wrapper was folded into a square of approximately 1 cm^2 (approximately the same size as the XRF shutter window). The wrapper was placed over the XRF analysis window so that the entire folded wrapper covered the entire XRF analysis window. An effort was made to keep the wrapper as flat as possible against the XRF analysis window. The wrapper was then analyzed and the results were recorded. The method was repeated for all 35 wrappers.

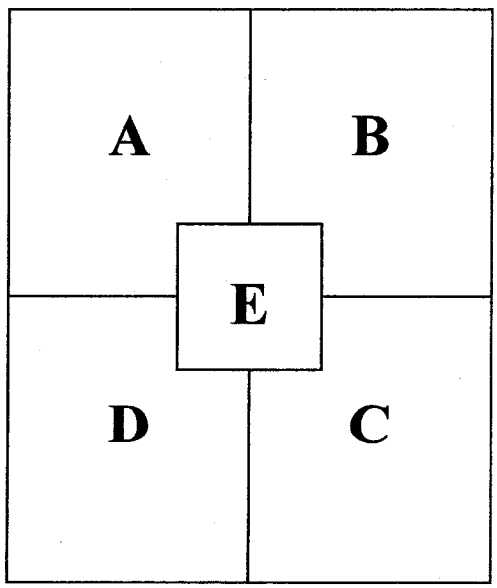

Figure 1 - Five Quadrants Method

Bulk Mode

The XRF was set to bulk sample mode with an analysis time of 60 seconds then placed in a protective holding stand provided by Niton Corp. The wrapper was removed from its protective container, crumpled up, and placed into a XRF soil analysis cup. The wrapper was then analyzed according to EPA Method 6200 (http://www.epa.gov/SW-846/pdfs/6200.pdf, 2006) and the results were recorded. The method was repeated for all 35 wrappers.

Dust Wipe Mode

The XRF was set to dust wipe mode then placed in a protective holding support provided by Niton Corp. The wrapper was removed from its protective container and folded up so that the entire wrapper was exposed in the window of the dust wipe analysis holder provided by Niton Crop. The wrapper was then analyzed according to the HUD Dust Wipe Analysis method (www.hud.gov) which involves rotating the wrapper so that the entire wrapper is analyzed completely and the results were recorded. The method was repeated for all 35 wrappers.

Wrapper Characteristics

An additional 780 candy wrappers that were collected from throughout the Las Vegas Valley were colleted and analyzed using the thin sample mode – single shot method as described above. The candy characteristics including manufacturer, wrapper color, candy type, and county of origin were recorded in a database. Wrappers were then analyzed to determine if there was a relationship between color and lead content. A minimum of 30 wrappers were selected. For wrapper colors with greater than 30 wrappers tested, a

random sample of 30 wrappers was taken from the total amount of wrappers tested from that color.

NIST Standards

NIST paint films were analyzed to better understand the possible effects of polymer coatings on lead content and whether or not these coatings could be removed in order to test chemical lead test kits.

Ninety-five paint films were obtained from NIST (Gaithersburg, MD) and were assigned unique identification numbers. Theses numbers were printed on each piece of the films when cut. A 2 cm reference strip was then cut from the bottom of each paint film and archived. The paint films were analyzed in the center of each of 4 quadrants as well as a 5^{th} location in center of the paint film where the four quadrants intersect (see Figure 3-1). The paint films were analyzed using a Niton XRF model XLp 303A using the Lead paint Mode option (mg/cm^2) prior to and after removing the polymer coating. Quality assurance and control was performed with certified lead standard provided by Niton Corp. The XRF was calibrated prior to testing, after every 50 measurements, and upon completion of testing. Instrument calibration was tested using standards provided by Nitron Corp. Calibration was performed by testing 3 separate lead standards 3 times each.

Polymer Delamination: The paint films were secured with a hemostat, and placed flat on a clean paper towel on the inside of a fume hood. One hand was used to hold the hemostat to keep the paint film in place and the other hand used to operate the heat gun. The heat gun (using the high temperature setting of approximately 120 degrees Celsius) was held approximately 3-4 cm away from the paint films and heat applied evenly to the

paint film for approximately 2-3 minutes at a temperature of 185 °C. After approximately 2-3 minutes of heating, heat from the gun was concentrated on one corner of the paint film in order to produce a small bubble or ripple. While concentrating on one corner, heat was also applied occasionally elsewhere on the paint film to maintain an even temperature on the polymer coating. When a small bubble or ripple was created on the corner of the paint film, tweezers were quickly used to peel away the polymer coating. The hemostat was then used to completely remove the polymer coating. If the polymer coating was not completely removed during the first attempt, the procedure was repeated on the remaining section(s) of the polymer coating. Post-peeled paint standards were stored in polyethylene Ziploc bags. The post-peeled standards were then sent to an independent lab for analysis using the Graphite Furnace Atomic Absorption Spectrometry (GFAAS).

CHAPTER 4

RESULTS

A Pearson's Correlation was used to compare XRF wrapper analysis method results with the results of Graphite Furnace Atomic Absorption Spectrometry (GFAAS). Table 4-1 shows the results of the Pearson's correlation. Thin Sample Mode – Four Quadrant & Middle has the highest correlation to the results of the Graphite Furnace Atomic Absorption Spectrometry (GFAAS), though all methods have a significant correlation to the results of Graphite Furnace Atomic Absorption Spectrometry. The hypothesis that the 4 Quadrant & Middle method would have the greatest correlation to the GFAAS was supported.

Table 3: Comparison of GFAAS to XRF Analysis Methods (n=35)

Mode	Method	r
Thin Sample	4 Quadrant & Middle	.992
Dust Wipe	Dust Wipe	.974
Thin Sample	Folded Wrapper	.972
Thin Sample	Single Shot	.969
Bulk Cup Mode	Soil	.921

A Chi-Squared test was used to analyze frequency of the presence of lead content by color of candy wrapper. The data are presented in Table 4-2 and 4-3. The distribution of wrapper color to lead content has a Chi-squared value of 16.976 and a P-value of .075 indicating that lead content is dependent on wrapper color. Hypothesis #2 was not supported in stating that lead content is independent of wrapper color.

Table 4: Distribution of Wrapper Lead Content to Wrapper Color (n=30)

χ^2	P
16.976	.075

Table 5: Wrapper Color and Wrapper Lead Content as Determined by XRF Testing.

Wrapper Color	Tested Positive	Number Tested	% Positive
Red	27	40	68%
Blue	18	30	60%
Green	26	50	52%
Purple	48	75	64%
Clear	130	200	65%
Pink	44	60	73%
Orange	42	65	65%
White	20	35	57%
Metallic	22	30	73%
Brown	18	30	60%
Yellow	98	165	59%

Candy characteristics such as candy type, manufacturer, and brand were recorded and are presented in Table 4-4, 4-5, and 4-6.

Table 6: Results of analysis for lead by candy type

Candy Type	Tested Positive	Number Tested	% Positive
Tamarind	110	160	69%
Hard Candy (suckers)	189	250	76%
Chilli	104	190	55%
Gum	8	20	40%
Soft Candy	82	160	51%

Table 7: Results of analysis for lead by country of origin

Manufacturer Location	Tested Positive	Number Tested	% Positive
Mexico	396	670	59%
Brazil	97	110	88%

Table 8: Results of analysis for lead by candy brand

Candy Brand	Tested Positive	Number Tested	% Positive
Dulces	180	320	56%
Lucas	50	100	50%
Fortuna	60	60	100%
Cima-Mex Corp.	20	30	67%
Candy Azteca	16	25	64%
Peccin	33	40	83%
Sherwood Brands	5	10	50%
Confivero	18	30	60%
Paletas mara	42	60	70%
Montes	43	60	72%
Bradford Fine Candies	12	20	60%
Channel	4	10	40%
De La Rosa	10	15	67%

A paired T-Test was used to determine lead concentration differences between pre-peeled and post-peeled lead standards. The results are shown in Table 4-4 and Table 4-5. Pre-peeled standards contain a mean concentration of lead of 1.1743 ug/cm^2 while post

peeled standards contain a mean concentration of lead of 1.2038 $\mu g/cm^2$. There was an r value of .672 with a significance of .019. There was no difference between pre-peeled and post-peeled NIST lead standards. Hypothesis #3 was supported in stating that pre-peeled and post-peeled NIST lead standards will have the same concentration of lead.

Table 9: Mean Comparison of Lead Concentration of Post-peeled vs. Pre-Peeled NIST Standards (n=95)

	Mean($\mu g/cm^2$)	Standard Deviation
Pre-peeled	1.1743	.11011
Post-peeled	1.2038	.10467

Table 10: Comparison of Lead Concentration in NIST Standards Following Removal of the Protective Coating (n=95)

	r	Significance
Pre-Peeled & Post-Peeled	.672	.019

CHAPTER 5

DISCUSSION

In today's highly globalized society, products manufactured half way around the world may be sold at a local supermarket. Product quality standards vary greatly between countries, and many countries do not have the same high product quality standards that the United States has, resulting in the importation of contaminated or unsafe products into the United States. Public health officials throughout the United States are confronted with determining the safety of an ever increasing array of products from a variety of countries. It is very important for public health entities to be able to rapidly and accurately determine safe and unsafe products. The development of screening methods that are timely, accurate, and cost effective, are needed to screen products for their safety.

One such imported product that has posed a public health risk is candy. Many types of candy are imported into the United States from around the world. Imported candy is particularly at risk for lead contamination and is consumed by a population that is highly susceptible to the detrimental health effects of lead exposure, children. It is important to detect unsafe products, while not eliminating those products which are safe.

The main considerations when choosing a method for screening is accuracy, time needed to complete the analysis, and the cost needed to complete the screening method. The screening method needs to be economical, accurate, and fast in order to test large

amounts of candy effectively. There are a wide variety of methods to test for candy in lead that are highly accurate, but are timely and expensive. The XRF provides screening methods that are quick and cost effective, but the XRF's accuracy with certain products such as candy and wrappers until this work was unknown. Further development of a proper XRF candy screening protocol is the key to providing an accurate, quick, and cost effective method to screen large quantities of candies.

The Thin Sample Mode – 4 Quadrant & Middle correlated the best with GFAAS, which is considered the gold standard for testing lead. In addition, the other four methods also proved to be correlated significantly with GFAAS. When determining the best method to use as a screening tool, though, correlation to GFAAS is not the only factor to consider. We must also consider the time needed for candy analysis and how well the method can be effectively repeated in the field. When taking these other factors into consideration, the best method to use as a screening method would be Thin Sample Mode – Single Shot. This method is highly accurate (r=.969) as well as easy to use and takes a considerable less amount of time than the other methods. The single shot method takes about $1/5^{th}$ the amount of time to conduct as the Thin Sample Mode – 4 Quadrant & Middle method with only a negligible accuracy when compared to GRAAS. The ease of use would also make this method very suitable to use in the field. A quick screening process is essential when screening large amounts of candy. The single shot mode greatly reduces time and sample preparation work allowing for a larger number of candies to be screened in a shorter period of time with only a minimal reduction in correlation to the graphite furnace. This would be the ideal method for screening candies on a large scale in the field.

It has been suggested that physical attributes such as color, country of origin, and/or manufacturer can be used to determine wrapper lead content. The data demonstrated that there was a relationship between wrapper color and wrapper lead content. However, this may not be a real representation of candy wrapper color since many of the colors were represented by a single brand or were of a particular candy type as shown in tables 4-5, 4-6, and 4-7. This may have skewed the results making it appear that there was a relationship between wrapper color and wrapper lead content. Furthermore, many of the clear wrappers, which did not have any color or markings, tested positive for lead content. This may point to the fact that lead is contained in the plastic rather than the ink or dye markings applied to the plastic. The plastic used by particular brands of candy may be contaminated with lead. Sample characteristics such as brand, wrapper color, and candy type should be recorded when analyzing candy wrappers in order to gain a better understanding of the role they play in candy and wrapper lead content. Candy brand and country of origin may be other determinants of candy lead contamination. Particular countries or brands may have plastic which is contaminated with lead and is used in the manufacturing of candy wrappers.

A better sampling method could be used to determine if wrapper color does play a role in determining wrapper lead contamination. A much larger sampling pool is needed with multiple manufacturers and brands for each candy wrapper. A random sample could then be taken and analyzed according to color. This would help better determine which wrapper attributes contribute to lead contamination.

Candy wrapper leaching may pose a significant threat to children's health, especially for wrappers with high lead content. The acidic nature of many of the candies may

enhance the leaching process, contaminating the candy with lead. In addition, young children may place candy wrappers in their mouths for extended periods of time, allowing the lead to leach out directly into the child's mouth. The ability of the lead to leach out of candy wrappers has not been widely studied, but is a crucial point when determining the safety level of candy wrappers which contain lead. Further study is needed to determine if lead leaching from contaminated candy wrappers poses a danger to human health.

Due to the fact that imported candy is widespread throughout the United States, not just the Southwest, a nationwide candy screening program is needed. Childhood lead screening programs are already in place in all 50 states. These programs already have access to XRF(s) and knowledgeable personnel who are experienced in using XRFs for lead detection. This would allow the startup cost of a nationwide lead screening program to be minimal. Once a standard protocol is developed, each States' lead program would be instructed on how to properly test candy for lead using the XRF. In addition, each state would be given instructions on which candy characteristics to record. Characteristics such as the date, the location, result of the test, the brand of candy, the manufacturer, the type of candy, and the lot number would be recorded. The data would then be entered into a centralized database via the internet by each state program. The central database would record and log information from each state as well as provide up to date information about the results of lead testing from throughout the country. In addition, candy testing results would be monitored by the centralized database operators. Regional, statewide, or countrywide warnings would be issued when certain candy tests positive for lead. Candies could be monitored by brand, manufacturer, or even country.

Manufacturers, brands, or countries of lead contaminated candies could be put on watch lists and continually monitored for lead contamination until deemed safe. A store monitoring program could be put in place that randomly screens candies at stores which sell imported candy. In addition, the database could be used for research projects and statistical analysis to provide a better understanding of candy lead contamination throughout the country.

Pre-peeled and post-peeled NIST standards have the same concentration of lead thus showing that they can be used to test the reliability of chemical lead test kits. The preliminary unreliability of the test kits reduces the likelihood that they can effectively be used to screen candy. Test kits suffer from the fact that it takes a significantly high concentration of lead for a product to test positive for lead. Furthermore, the lead must be readily available on the surface of the product which reduces the effectiveness of the lead test kits, especially when testing candy. The lead test kits are also unable to quantify the amount of lead contained in a product and only give a positive or negative result. These test kits proved highly unreliable when compared to the XRF or other testing methods. The post-peeled NIST standards can be used in further study of the test kits in hopes of developing a method that is better able to determine lead concentration.

Conclusion

Further testing is needed to better understand the best techniques and methods for using the XRF to screen for lead in candy. The different and unique attributes of candy and candy packaging create a unique challenge for screening for lead using an XRF. Further study to determine the best methods for detecting lead in the candy itself and other types of candy packaging materials such as straws, spoons, and containers will

prove necessary. Each type of candy product and packaging provides a unique challenge while testing with the XRF.

This research examined several possible techniques for analysis of candy wrappers and indicates which ones should be studied further in order to develop a candy testing protocol which can be implemented nationwide. When a final testing protocol is developed, the XRF will provide an economical, quick, and accurate method to screen candy. Many lead programs throughout the nation already have XRFs and trained personnel to use them. Lead programs can be expanded to screen candy almost immediately after a XRF screening protocol is approved. This will provide the much needed vigilance in protecting the children from lead contaminated candies.

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