Deanship of Graduate Studies

AL-Quds University

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Ahmad Abdelqader Al-asafrah

M. Sc. Thesis

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By

Ahmad Abdelqader Al-asafrah

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3) - Internal Examiner: Prof. Hasan Dweik Signature----------------

Jerusalem - Palestine

2013

Dedication

“To Our Profit Mohammad

(Peace be upon him)”.

“To my Family and Friends”

Declaration

I Certify that this thesis submitted for the degree of Master of Science is the result of my own research, except where otherwise acknowledged, and that this thesis (or any part of the same) has not been submitted for a higher degree to any other university or institution.

Signed……………….
Ahmad Abdelqader Al-Asafrah

Date / / 2013

Acknowledgement

Thanks to Allah, who gave me strength, determination, perseverance, and patience to complete this research .Peace and blessings be upon the first teacher and professor of all human beings Mohammed bin Abdullah.

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Abbreviations

ATSDR	**Agency for Toxic Substances and Disease Registry**
CMR	**Carcinogenic Mutagenic Substances Toxic to Reproduction**
CPSC	**Consumer Product Safety Commission**
EC	**European Commission**
EFSA	**European Food Safety Authority**
EU	**European Union**
GTF	**Glucose Tolerance Factor**
IARC	**International Agency for Research on Cancer**
ICPMS	**Inductively Coupled Plasma Mass Spectrometry**
IPCS	**International Program on Chemical Safety**
ISO	**International Organization For standardization**
IUPAC	**International Union For Pure And Applied Chemistry**
MAL	**Maximum allowable limit**
MARS	**Microwave Accelerated System**
NYPGIR	**New York Public Interest Research Group**
OSHA	**Occupational Safety and Health Administration**
PSI	**Palestinian Standard Institute**
PVC	**Poly vinyl chloride**
TDI	**Tolerable Daily Intake**
TTLC	**The Elemental Threshold Limits Concentrations**
UNEP	**United Nations Environmental Program**
USEPA	**United States Environmental Protection Agency**
USFDA	**United States for Food & Drug Administration**
WHO	**World Health Organization**

Abstract

Children exposure to heavy metals continues to be a major health concern. This study examined heavy metal content in children's toys made of plastic purchased from local markets in Palestine. Fifty plastic made toys were analyzed to determine the concentration of heavy metals (Pb, Cd, Cr, Hg, As, Se, Ba, and Zn) in these toys. Toy samples were randomly selected from products available in the shops, stalls and hawkers in Hebron, Ramallah and Nablus markets in Palestine. The toy samples were tested for PVC before analysis. Eighty percent of the toys samples tested were positive for PVC. After digestion of samples with concentrated nitric acids HNO_3 and hydrogen peroxide H_2O_2 using a Microwave digester. The concentrations of the selected heavy metals were determined by using Inductively Coupled Plasma Mass Spectrometry or ICP-MS spectrophotometer (Agilent 7500).

The result showes that the presence of heavy metals in the toys were in the range of **(0.76 - 8195.6), (0.47- 436.42), (6.76 – 2468.0), (0.118 - 85.9), (1.04 - 2486), (16.6 - 2833), (6.76-9159.0) and (9.5 - 7526.80)** mg/Kg for Pb, Cd, Cr, Hg, As, Se, Ba, and Zn respectively. Both PVC and non-PVC toys contain heavy metals but the concentration of these metals in non-PVC toys are generally less than that of PVC toys. The present study reveals that **42%** of the toy samples show high concentration (above international limits) for Lead, **30%** for Cadmium, **34%** for Chromium,**6%** for Mercury, **42%** for Arsenic, **32%** for Selenium, **20%** for Barium and **40%** for Zinc.

On the other hand, Seventeen plastic made toys were purchased from Israeli markets for comparison. The concentrations of heavy metals in these seventeen toy samples were measured and compared with their Palestinian counterparts. Concentrations of heavy metals in the Israeli toys ranged from **(2.8 to 95.5 ppm)** for lead with an average equal to **39.2** ppm and from **(4.5 to 75.1)** with an average equal to **36.9** for cadmium, and from **(7.15 to 59)** with an average equal to **36.87** for chromium, and from **(3.2 to 25)** with an average equal to **3.62** for mercury**,** and from **(0.0 to 22.4)** with an average equal **4.95** for arsenic, and from(**0.71 to 342**) with an average equal to **93.9** for Selenium, and from **(14 to 489)** with an average equal to **156.29** for barium, and finally from (**16 to 500**) with an average equal to (**159.56**) for zinc. The result found that **94.5%** of the Israeli samples are safe, and their concentrations were less than the maximum internationally allowable limits.

In the same context, ten toy samples (**2.5**gm each) have been crushed and dipped for **8** hours in a solution of artificial saliva (**20**ml). The solution was acidified and tested for heavy metal concentrations, but none of the dipped samples resulted in migration concentrations of heavy metals exceeded the international maximum allowable limit.

In general these high levels of heavy metals concentrations, found in the plastic toys in the Palestinian markets formed a health hazard to children and put their lives at risk. Overall the study findings revealed a valuable data that can be used to provide a clear picture of hazardous metals in plastic toys purchased from the Palestinian markets.

Accordingly, and in light of the above, we recommend the competent authorities to take the following actions:

1) - Act quickly to adopt policies to protect consumers and stop importing of PVC made toys and other children's products.

2) - Eliminate the purchase of products and packaging that contain lead, cadmium, and other hazardous heavy metals and chemical additives in toys and children's products.

3) - Label the material content of toys so that consumers can easily identify safer products. Toys made with PVC should be labeled "made with PVC." Toys made without PVC should be labeled "PVC-free." By requiring all PVC products to be labeled, consumers can readily identify which products contain PVC and its additives and which are safe to purchase.

3) - Monitor the use of toys by the children, and reduce their chewing and sucking the toys especially those made of PVC.

Chapter One

Introduction and Related Studies

1. Introduction

1.1 Rational of the Study

Heavy metals are inorganic chemicals which are added to a wide variety of PVC (polyvinyl chloride) made toys, in order to provide the necessary stability, and to impart some characteristics such as softness, brightness, and flexibility to those products.

There exists a concern that heavy metals can migrate from soft PVC toys, where these are chewed and sucked by children and thus pose toxic effects in the long term. The toxic elements that may be present in toys are heavy metals such as lead, cadmium, arsenic, chromium, selenium, mercury, etc., which can accumulate in the body and may cause adverse effects. Therefore, analysis of such elements and preventive action is important to ensure safety.

Toys safety is a joint responsibility among governments, manufacturers, regulatory bodies and parents. The responsibility is multiplied, in the areas that live difficult economic and harsh occupying circumstances such as the Palestinian case, where censorship and laws are completely absent and off. We have to keep in our minds that companies, facing fierce competition, simply could not be trusted to police themselves. The flow of unidentified cheap and poor quality of children toys on the Palestinian markets makes one suspects that these toys may be sold or may be reached these markets via suspicious channels. These channels can both refer to raw materials manufacturing outside the oversight of regulators (small domestic companies in an “un organised sector” over which public authorities have little control) or to distribution (toys distributed without required or legitimate documentation). Compliance with respective regulatory frameworks is questionable in many of these cases. Likewise, information on chemicals in toys produced and distributed through these channels seems to be non- existent.

Many organizations and concerned bodies warned of the danger of heavy metals contaminated plastic toys (NYSPPI, 2010; NPI 1999 & 2001).

The popular outcry against PVC-made toys swept most of the civilized countries of the world and some of them took practical steps such as the United States which has recalled of an estimated 20 million Chinese-made toys by Mattel on August 14, 2007 (CFA, 2008).

If these deadly products reached markets of very advanced countries, that has the potential of technical, material and has a system of laws, legislation and strict control. Is it conceivable that our Palestinian markets are fortified against them?! We firmly believe not. If we remain silent on this matter, the problem will become more complicated, and the generation of babies will be born pre-polluted with potentially harmful levels of heavy metals that may possibly cause lifelong health problems. For all these reasons, it was necessary to conduct like this study.

1.2 Definition and importance of toys

The term **toy** according to EU Directive no. 2009/48/EC means "any product that exclusively or partly is designed or intended to be used during play by children under the age of 14 years".

Toy plays a vital role in the growth and development of children. It has been considered to be an integral part of child development. Toy promotes their behavioral skills, improves learning skills, and also helps support their creative abilities. It also helps the growth of their emotional and social well-being and gives them the opportunity to interact with other children (Ginsburg. 2009). For children with disabilities, toys are not only a wonderful educational tool, but they can provide a unique opportunity for communication, self expression, and they like their counterparts from healthy children. On the surface, children playing with a toy seem simple, but in fact, they are learning a skill each time they play. Playing with toys can set the foundation for reading, writing; mathematical reasoning, social interaction, and creativity, toys are integral part of children developmental processes (Clouder, 2007).

1.3 Toys made of Plastics

In this study we were interested in children toys made of plastic polymer. Currently, plastics are used in more than 80% of all new toys (Hall, 2003)**.** In many aspects, plastic materials are cheaper, easier to process (can be bend and mold under reasonable temperatures), and have more color possibilities than the conventional toy making materials like clay, metals, ceramic, and wood. There are many polymers, used in manufacturing the toys. The use of any polymer depends on the type of toy and the purpose for which it is made.

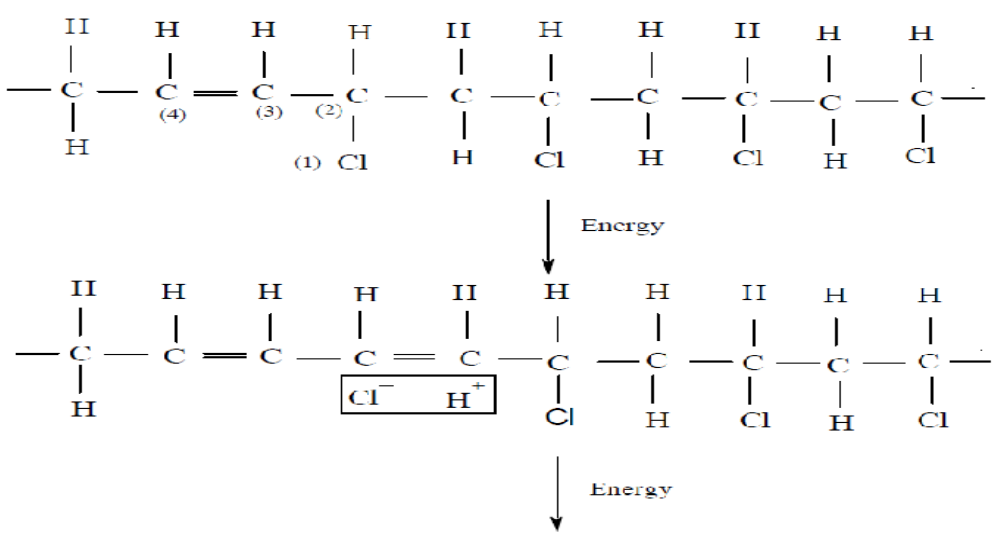
Polymers contain a wide variety of additives (plasticizers, antioxidants, stabilizers, coloring agents etc.) to fulfill their physical and chemical properties.

Environmental problems can be associated with all kinds of plastics, from production to disposal (Costner, 1997); however, PVC has the greatest impact on the environment and on health throughout its lifecycle. It represents the worst plastic, from both an environmental and health standpoint. Due to its negative environmental and health impacts, this study focused on toys made of PVC plastic polymer.

PVC (poly vinyl chloride) plastic is used to manufacture many consumer products, including children's toys and infant products. The use of PVC in toys requires the addition of some heavy metals as stabilizers such as, lead, cadmium, arsenic, chromium etc... Without these additives, it's not possible to use PVC to make toys or other children's product. Since the additives are not chemically bound to the PVC in toys, they can migrate from within the toys to the surface (Wallis, 2009). In turn, children may be exposed to these hazardous substances by playing with, chewing, or sucking the toys.

1.4 Mechanism of stabilizers

The poor thermal stability is one of the most serious problems for PVC polymer, so it is widely accepted that PVC, is an unstable polymer when exposed to high temperatures during its moldings and applications. The main indicators of thermal degradation of PVC are the evolution of hydrogen chloride, development of color (from light yellow through reddish brown, to almost black in severe cases) and deterioration of physical, chemical and electrical properties. It is widely accepted that dehydrochlorination (DHC) involves progressive unzipping of neighboring chlorine and hydrogen atoms along the polymer chain; a double bond is formed between the carbons to which the two atoms were originally attached (Hjertberg, 1988). This constitutes an allyl chloride structure with (i.e. in the 3, 4 position) the next Cl down the chain, which is thereby strongly activated and so on (Titow, 1985).



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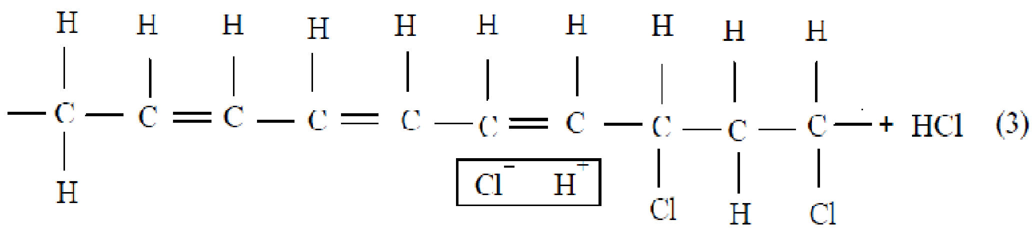

Allyl chloride structure

Source **(**Folarin and Sadiku 2011)

The development of color is due to the conjugated double bond systems formed in this process. The process starts with a chlorine atom activated by an adjacent allylic bond configuration where that is already present in mid-chain (3).

Dehydrochlorination can occur at only moderately elevated temperatures (about 100°C). It is catalyzed by the HCl evolved (autocatalysis), and can also be promoted or initiated by other strong acids. In addition to dehydrochlorination, thermal degradation of PVC polymer in the presence of oxygen also involves oxidation, with the formation of hydroperoxide, cylic peroxide, and keto groups, some of which can provide additional active sites for initiation of dehydrochlorination (William, 2011)**.** These effects contribute to the general deterioration in properties. Accordingly it has become the practice to process PVC in the presence of heat stabilizers, it has become impossible to manufacture with good specifications without thermal stabilizers.

The function of thermal stabilizers for PVC can be summarized as "they replace labile chlorine atoms in the polymer; they modify chain reactions and thereby inhibit the elimination of hydrogen chloride and interrupt the formation of polyene sequences in the polymer" (Arkis and Balkose, 2005).

1.5 Environmental impacts of PVC as toys matrices

The lifecycle of PVC, from manufacturing to use and disposal, releases hazardous chemicals including chlorine gas, vinyl chloride, ethylene dichloride, dioxins and furans, mercury, lead, phthalates, cadmium and organotins that are toxic to children's health and the environment. As a result of this contamination, babies today are born pre-polluted with potentially harmful levels of dioxins in their body (Costner, 2001). Chemicals released in PVC's lifecycle have been linked to chronic diseases that are on the rise, including breast cancer, learning and developmental disabilities, and reproductive health problems (Lester and Belliveau 2004).

1.6 Definition of heavy metals

The term heavy metal is an ambiguous term, and there is no consensus among scientists on a clear and specific definition of it. Its definition is not existed in any inorganic chemistry textbooks, and never defined in the nomenclature by even authoritative International Union of Pure and Applied Chemistry (IUPAC) (Duffus, 2002). But the most famous and widespread definition is: “heavy metals are a group of elements relatively high density and is toxic or poisonous even at low concentration” (Rand, 1995).

1.7 Bioimportance of heavy metals

Some heavy metals (like, Zn, Ca and Mg) are of bio-importance to man (Mildvan, 1970). While, some others (like As, Cd, Pb, Se, Cr [V1], Sb, and methylated forms of Hg) have no known bio-importance in human biochemistry and physiology and consumption even at very low concentrations can be toxic (Hogan, 2010). “Even for those that have bio-importance, dietary intakes have to be maintained at regulatory limits, as excesses will result in poisoning or toxicity, which is evident by certain reported medical symptoms that are clinically diagnosable”, (Duffus, 2002).

1.8 Sources of heavy metals

There are two basic sources of heavy metals:

Natural sources such as: seepage from rocks into water, volcanic activity, forest fires etc. Anthropogenic sources such as; mining, smelting and metallurgical industry, plastic toys, chemical industry, textile printing and dyeing, leather tanning, pesticides, animal feed manufacturing, electroplates, and batteries, etc.. (Herawati, 2000).

1.9 Health effects of heavy metals

Heavy metals are responsible for a very wide range of different illnesses. Heavy metal toxicity can result in damaged or reduced mental and central nervous function, lower energy levels, and damage to blood composition, lungs, kidneys, liver, and other vital organs" (McLaughlin,1999). Long-term exposure may result in slowly progressing physical, muscular, and neurological degenerative processes that mimic Alzheimer's disease, Parkinson's disease, muscular dystrophy, and multiple sclerosis. Allergies are not uncommon and repeated long-term contact with some metals or their compounds may even cause cancer.

Heavy metals can be responsible for a range of health effects such as "cancer, neurotoxicity, immunotoxicity, cardiotoxicity, reproductive toxicity, teratogenesis and genotoxicity" (HEI, 1998; US EPA, 1999) .The most affected generation is the generation of kids "Children are not "little adults"—their developing brains and bodies, their metabolism and behaviors make them uniquely vulnerable to harm from toxic chemicals such as those released by the PVC made toys lifecycle" (EPA, 2003). The following section discusses in some detail each of these elements and identify the characteristics and health detriments.

1.10 Selected elements and their toxicity

1.10.1 Lead (Pb): A soft, malleable, ductile, bluish-white, dense metallic element. With atomic number 82, symbol Pb, atomic Mass: 207.2 amu, melting Point: 327.5 °C - 600.65 °K, boiling point: 1740.0 °C - 2013.15 °K and density 11.34 g/cm3.

Lead is used as a heat stabilizer and pigment in PVC made toys. According to the Vinyl Institute PVC, digestion, inhalation and skin contact with lead occurs every day, and the routine handling of toys and inexpensive jewelry containing high levels can be evidenced to be distributed throughout the body (Rastogi & Clausen, 1976; Lilley, 1998). When a child puts an object containing lead in his or her mouth, the child can suffer seriously from lead poisoning (Sprinkle, 1995). In the body, lead will either accumulate in tissues, especially bone, or in organs such as liver, kidneys, pancreas, and lungs. Fetuses and young children are particularly vulnerable because lead can cross the placenta with ease and enter the fetal brain (Campaign for Safe Cosmetics, 2007).

Lead exposure has been linked to IQ deficits, miscarriage, hormonal changes, reduced fertility in men and women, menstrual irregularities, delays in puberty onset in girls, memory loss, mood swings, nerve, joint and muscle disorders, cardiovascular, skeletal, and kidney and renal problems (Environmental Working Group, 2010).

1.10.2 Cadmium

Cadmium: A solid bluish-white "Transition Metal" element which is located in Group 2B of the periodic table. Generally described as ductile, malleable, and able to conduct electricity and heat. The element symbol is Cd, atomic number 48, atomic mass 112.411amu, melting point: 320.9 °c, boiling Point: 765.0 °C, density 8.65 g/cm3 (Holleman , 1985). Cadmium and Cadmium compounds are mostly used to make nickel-cadmium batteries and as stabilizers to prevent degradation of PVC from heat and light and this process is taken place as follows: Mixed metal soaps like barium/cadmium, barium/zinc, and calcium/zinc act as stabilizers by replacing reactive chlorine atoms with less reactive atoms or groups (Tuczai, E., Cortolano, F, 1992). In a barium/cadmium soap a carboxylate group substitutes for chlorine which reacts with cadmium forming cadmium chloride. The cadmium chloride then reacts with barium forming barium chloride and regenerating the cadmium metal soap, (Tuczai, E., Cortolano, F, 1992). But after the year 2000 the stabilizer industry is now based on barium/zinc (Ba/Zn) or calcium/zinc (Ca/Zn) systems and the change has occurred over a 15 year period and in March 2001 all use in the EU has ceased (MarceloE..Conti, 2008).

Cadmium and its compounds are also found in various pigments used to color PVC products specially PVC made toys (ATSDR 1999).

Cadmium is absorbed into the body and accumulates in the kidney and the liver, although it can be found in almost all adult tissues (Elinder, 1985). Cadmium and its compounds are considered to be “carcinogenic to humans” by the IARC (International Agency for Research on Cancer, 2010) and are considered “toxic” in Canada because of their carcinogenicity and environmental effects (Environment Canada & Health Canada, 1994a). Cadmium and its compounds are also classified as known human carcinogens by the United States Department of Health and Human Services (Agency of Toxic Substances and Disease Registry, 2008).

1.10.3 Mercury

Mercury is a heavy, silver-white metal that exists as a liquid at ambient temperatures. Its chemical symbol, Hg, comes from the Latin word, hydrargyrum, meaning liquid silver. Atomic weight 200.59, atomic number 80, valences 1, 2, melting point, EC -38.87boiling point, EC 356.9, density,13.546 g/cm3 (DeVito, 1995).

Most of the mercury in the environment results from human activity, particularly from coal-fired power stations, residential heating systems and waste incinerators. Mercury is also present as a result of mining for mercury, gold (where mercury is used to form an amalgam before being burnt off), and other metals, such as copper, zinc and silver, as well as from refining operations (IPCS, 1990). Mercury is used as a catalyst to spark the chemical reaction among ingredients in manufacturing of PVC from coal in china.

Elemental and methyl mercury are toxic to the central and peripheral nervous system. The inhalation of mercury vapor can produce harmful effects on the nervous, digestive and immune systems, lungs and kidneys, and may be fatal. The inorganic salts of mercury are corrosive to the skin, eyes and gastrointestinal tract, and may induce kidney toxicity if ingested (SRI International, 1996).

Children are especially vulnerable and may be exposed directly by eating contaminated fish (Goldman ,2001). Bioaccumulated in fish and consumed by pregnant women may lead to neurodevelopmental problems in the developing fetus. Transplacental exposure is the most dangerous, as the fetal brain is very sensitive (Goldman, 2001).

Note * PVC manufacturing consumes over 800 metric tons of mercury every year.

* Chinese PVC manufacturing industry is one of the most significant uses of mercury in the world today. c

1.10.4 Arsenic

A highly poisonous metallic element with atomic number 33; atomic weight 74.922; valence 3, 5. Gray arsenic melts at 817°C (at 28 atm pressure), sublimes at 613°C, and has a specific gravity of 5.73 (Biberg et. al. 2001). Arsenic is a metal that naturally occurs in the earth’s crust and may enter water sources naturally (ATSDR, 2007a). Arsenic and its compounds are used as insecticides, weed killers, and in various alloys and products including textiles, preservatives, and pigments (Health Canada, 2010).

Arsenic and its inorganic compounds are considered to be “carcinogenic to humans” by the International Agency for Research on Cancer (IARC, 2010). Inhalation includes some of the skin effects, circulatory and peripheral nervous disorders, an increased risk of lung cancer (ATSDR, 2007a), and a possible increase in the risk of gastrointestinal tract and the urinary system cancers (Gibb & Chen ,1989). Long-term skin contact is not likely to lead to any serious internal effects (ATSDR, 2007a).

1.10.5 Selenium

Selenium is a chemical element with symbol Se and atomic number 34. It is a nonmetal with properties that are intermediate between those of its periodic table column-adjacent chalcogen elements sulfur and tellurium (Emsley, 2011). It rarely occurs in its elemental state in nature, or as pure ore compounds. Selenium Melting Point is 217 °C, Boiling point is 685 °C, and Density is 4.39g /cm3, (David, 2002). Selenium is also an essential nutrient required for the maintenance of good health (ATSDR, 2010). It is used in various electrical applications, as well as a colourizing and decolourizing agent for glass and to develop red, orange, and maroon (a dark red to purplish-red colour) pigments for ceramics, glazes*, plastic made toys, enamels, and paints, with the latter generally restricted because of its toxicity (Health Canada, 2010b). It may also be found in stainless steel, enamels, inks, rubber, pesticides, fungicides, batteries, explosives, and some therapeutic shampoos (e.g., anti-dandruff) or lotions (e.g., anti-fungal) (Health Canada, 2010b). High levels of exposure over time can cause brittle hair and hair loss, brittle and deformed nails, and neurological abnormalities (ATSDR, 2010). In rats selenium has been shown to have reproductive effects (e.g., decreased sperm counts, increase abnormal sperm levels, reproductive cycle change) (ATSDR, 2010). Meanwhile high acute levels of exposure can result in nausea, vomiting, and diarrhea (Health Canada, 2010b), with skin contact causing rashes, redness, heat, swelling, and pain (ATSDR, 2010).

Note* glazes means a vitreous coating to a ceramic material whose primary purposes are decoration or protection

1.10.6 Zinc

Elemental zinc is glossy, blue-white to grey metal that is virtually insoluble in water. It has a melting point of 419.5°C and boiling point of 908°C (ATSDR, 1995). The primary anthropogenic sources of zinc in the environment are from metal smelters and mining activities (ATSDR, 1995). The production and use of zinc in brass, bronze, die castings metal, alloys, rubbers, and paints may also lead to its release to the environment through various waste streams**.** Barium-zinc stabilizers have found use in plasticized compounds, replacing barium-cadmium stabilizers. These are used in moldings, profiles, toys and wire coatings. Cadmium use has decreased because of environmental concerns surrounding certain heavy metals. Calcium-zinc stabilizers are used in both plasticized PVC and rigid PVC For food contact where it is desired to minimize taste and odor characteristics. Applications include meat wrap, water bottles, toys and medical uses. The essentiality of zinc was established over 100 years ago. Zinc is essential for the function of more than 300 enzymes, (Vallee and Falchuk 1993; Sandstead, 1994). Increased zinc consumption, has been associated with changes in health effects in humans, including decreased copper metalloenzyme activity (Fischer et.al. 1984; Samman and Roberts, 1987, 1988; Yadrick et.al. 1989; Davis et.al. 2000; Milne et.al. 2001).

Taking too much zinc into the body through food, water, or dietary supplements can also affect health. The levels of zinc that produce adverse health effects are much higher than the Recommended Dietary Allowances (RDAs) for zinc of 11 mg/day for men and 8 mg/day for women (ATSDR, 2005). If large doses of zinc (10–15 times higher than the RDA) are taken by mouth even for a short time, stomach cramps, nausea, and vomiting may occur. Ingesting high levels of zinc for several months may cause anemia, damage the pancreas, and decrease levels of high-density lipoprotein (HDL) cholesterol, (ATSDR,2005).

1.10.7 Chromium

Chromium is a chemical element which has the symbol Cr and atomic number 24. It is the first element in Group IVB. Chromium is a blue- gray metal that can be polished to achieve a high shine (Kalbus , 1991). It is extremely lustrous and while it is relatively hard, it is also very brittle. Chromium compounds are toxic. Chromium has many applications. It has been used in dyes to act as a mordant, which will permanently fix dyes to different fabrics. Chromium has also been used in paints as pigments. This is because chromium exhibits many different colors including; black, gray, green, blue, violet, orange, yellow and red, depending on the compound (Kalbus , 1991).

"Cr (III) in its biologically active form (glucose tolerance factor, or GTF, a dinicotinato-chromium[III] glutathione-like complex), facilitates interaction of insulin with its receptor site, influencing glucose, protein, and lipid metabolism" (US EPA, 2008). Thus, Cr (III) is essential for animals and human beings. Inorganic chromium compounds do not have insulin-potentiating activity. Chromium deficiency may cause changes in the metabolism of glucose and lipids. In some studies, dietary supplementation with chromium reversed changes in glucose tolerance and serum lipids (US EPA, 2008).

Cr (VI) is considerably more toxic than Cr (III). Some Cr (VI) compounds (such as potassium tetrachromate and chromic acid) are potent oxidizing agents, and are thus strong irritants of mucosal tissue. Effects included metabolic acidosis, acute tubular necrosis, kidney failure, and death (Saryan and Reedy, 1988). It can cause also oral ulcers, diarrhea, abdominal pain, indigestion, vomiting, leukocytosis, and presence of immature neutrophils. Effects data for lower exposure doses were not available (Zhang and Li ,1987). (OSHA, 2006)

Such effects include reddening of nasal mucosa, nasal irritation (ulceration, perforation), changes in pulmonary function, and renal proteinuria. Many of the available studies lack quantitative concentration-response data on chromium health effects suitable for quantitative risk assessment (ATSDR, 2001).

1.10.8 Barium

Barium is a soft silvery-white metallic element belonging to the alkaline earths with an atomic number of 56, an atomic weight of 137.34, valence 2, relative density 3.5g/cm^3, melting pt 729°C, boiling pt. 1805°C. It belongs to group IIA of the periodic table. Barium enters the environment through the weathering of rocks and minerals and through anthropogenic releases. Barium metal is mostly used as a "getter" to remove the last traces of gases from vacuum and television picture tubes (ATSDR, 1992).

The process of getter is to overcome a specific hurdle which arises during the production of sealed glass tubes. How can an oxygen-free vacuum be produced to extend the life of the filament? The answer is to remove residual gases by heating a metallic disk, known as a getter; inside the bulb. The getter is coated with Barium, which has an extremely high affinity for oxygen and nitrogen. After the bulb has been pumped down and sealed, the getter is heated to vaporize or "flash" the barium for maximum dispersion, and "get" any residual gas within the tube. (US EPA, 1985a). It is also used to improve performance of lead alloy grids of acid batteries; as a component of grey and ductile irons; in the manufacture of steel, copper and other metals; as a loader for paper, soap, rubber and linoleum, manufacture of hydrogen peroxide bleach, in dyes, in electroplating and metallurgy. Barium chlorate is used in fireworks, explosives, matches, and as a mordant in dyeing (Miner, 1969; Brooks, 1986).

Ingesting high levels of soluble barium compounds, has resulted in difficulties in breathing, increased blood pressure, changes in heart rhythm, stomach irritation, brain swelling, muscle weakness, and damage to the liver, kidney, heart, and spleen (ATSDR, 2007), EPA has found barium to potentially cause gastrointestinal disturbances, hypertension, and muscular weakness. There is no evidence that barium has the potential to cause cancer from lifetime exposures in drinking water (ATSDR, 2007).

1.11 Related works in the region and around the world

Because of their high toxicity and accumulation in biota, the environmental damage caused by its non-biodegradable and their effect on children health, many studies have investigated the occurrence and monitoring of heavy metals in plastic made toys. This subject had received considerable attention in some countries around the world. Unfortunately, there are no studies in the Arab region or in the Middle East in this regard nor any study in measuring the concentrations of the eight heavy metals together except one study that will be addressed later. Some of the important documented contributions relevant to the present study are as follows:

In Nigeria eight heavy metals concentrations in a number of toy samples, that were imported from China, was measured (Omolaoye . et.al. 2010). The concentrations of the heavy metals in the toys ranged from 2.50 -1445.00, 0.50 - 373.33, 31.17 - 119.67, 12.00 - 93.67, 266.67 -

2043.33, 5.00 - 191.67, 1.00 - 73.33 and 6.17- 36.67 μgg-1, for Pb, Cd, Ni, Cu, Zn, Cr, Co and Mn respectively. Both PVC and non-PVC toys contain heavy metals but the levels of these metals in non-PVC toys were found less than that of PVC toys. The study reveals that 17% of the toy samples show high concentration (above USFDA limit) of Lead, Cadmium, Chromium and other metals that had been determined (Omolaoye J. A. Uzairu A. and. Gimba C. E,2010). In another investigation Sindiku and Osibanjo has measured the concentration of lead, cadmium, chromium and nickel in plastic toys imported to Nigeria. The results obtained show that lead cadmium, chromium and nickel were high and ranged from 28.5 to 12600 mg/kg Pb, 0.15 to 9.55 mg/kg Cd, 1.30 to 394.50 mg/kg Cr, and 5.9 to 1911 mg/kg Ni. A comparison of the mean concentration of these metals in the analyzed toys sample showed the following pattern: Pb>Ni>Cr>Cd. The elemental concentration threshold limits concentration (TTLC) of 90, 75 and 60 mg/kg for lead, cadmium and chromium respectively (Sindiku and Osibanjo, 2011).

In a study conducted in India for investigation the concentration of lead and cadmium in soft toys. A total of 88 samples (77 PVC and 11 non-PVC) were analysed for lead and cadmium. The range for lead concentration in the tested samples was 0.65 ppm to 2104 ppm. For cadmium, it ranged from 0.016 ppm to 188 ppm(David Gutierrez, 2008). Out of 30 samples analysed for total concentration of Pb and Cd in toys brought from Mumbai, eight samples showed concentration higher than 200 ppm. Five samples (close to 20 percent of Mumbai samples analysed) showed very high lead concentration (from 878.6 ppm to 2104 ppm) even exceeding the US EPA limit of 600 ppm in painted toys (David Gutierrez 2008). A recent study has found the following ranges for toys exported to India: 0.219-1.12, 0.005-0.110, 0.251-1.090, 0.119-1.111, 0.219-1.040, 0.000-0.531 and 0.990-1.070 (ppm) for Pb, Cd, Ni, Zn, Cr, Co and Mn respectively. A comparison of the mean concentrations of these metals in the analyzed toys showed the pattern: Pb > Zn > Ni > Mn > Cr > Co > Cd. (Naseem , 2012).

In a study conducted by Stinger et.al. 2001, Cadmium was present in 19 samples, of which 18 were PVC. Among the PVC samples, the maximum level of cadmium detected was 230 ppm found in a drawer liner from the USA, while plastic pants from New Zealand contained 132 ppm. Both products contained cadmium in excess of the 100ppm maximum level set for PVC products in Europe. Lead was detected in 26 samples, of which 21 were PVC. However, the most interesting result was discovered in a non-PVC product from the USA which contained 5220ppm of lead. Among the PVC samples the maximum level of lead detected was from Chilean wallpaper which contained 441mg/kg of lead (Stinger et.al. 2001).

In Day Care Center in the Las Vegas Valley, an evaluation of plastic toys for lead contamination was conducted (Joseph Alan Greenway I, 1986). More than 500 sample toys were tested. Twenty nine contained lead in excess of 600 parts per million (ppm). Of those 29, 20 were PVC and 17 were yellow. In addition to examining lead contamination, the presence of other heavy metals was observed. It was found that when lead was elevated, there was a high probability (P = 0.72) of the presence of elevated concentrations (> 100 ppm) of the other heavy metals cadmium, arsenic and chromium (Joseph A. Greenway, 1986).

In its last report of 2009, which was prepared by “The Toxics in Packaging Clearinghouse” and submitted to the U.S. Environmental Protection Agency Under Assistance Agreement No.X9-97160301-0 To the Northeast Recycling Council, Inc. The report shows that 43% of the Packaging samples which were frequently used to package home furnishings, pet supplies, cosmetics, and inexpensive toys contain higher levels than is permitted internationally of lead and cadmium, 19 of 44 samples were made from flexible PVC Lead was detected in one-third of the failed packaging samples. The types of packaging materials that contained lead in this study were more diverse than those containing cadmium. The concentration of lead ranged from 122 ppm to 1503.88 ppm. The lead concentrations in PVC were on the lower end, generally falling below the median concentration (450 ppm), while lead in inks and colorants was more often detected at concentrations above 1500.00 ppm.

New York Public Interest Research Group**,** NYPGIR’s report, Treacherous Toys: Dangerous and Toxic Toys on New York’s Store Shelves, was written by Tracy McCabe Shelton, Esq., and Megan Ahearn, NYPIRG Program Coordinator Issued in December 2012. Shows that toys with high levels of toxic substances are still on store shelves, including toys which contain phthalates, as well as toys with lead content above the 100 parts per million limits.

In 2007, child product recalls reached 45 million toys and other children’s products,”. Over 30 million of the recalled units were toys. Popular toy manufacturers, such as Mattel*, were forced to recall millions of units due to problems associated with their products' lead paint violations or dangerous small magnets media to dub 2007 the Year of the Recall (Kids In Danger, 2008) . Over 17 million toys were recalled because they violated the federal Pb paint standard (Morrison, W. M). In January 2010, the CPSC recalled 55,000 units of children's costume jewelry that contained high levels of cadmium (Cd) (Kids in Danger, 2008). In June 2010, 12 million promotional drinking glasses sold at McDonald's were recalled because the painted coating contained Cd (Kids in Danger, 2008)

However and according to our best knowledge, I have not come across any study conducted on the analysis of heavy metals in toys export to Palestine.

Note *Mattel, Inc. is a toy manufacturing company founded in 1945 with headquarters in El Segundo, California.

1.12 Objectives of the study:

The main objectives of this study are:

1)- To asses and measure the concentration of eight heavy metals (lead , Cadmium , mercury , arsenic , chromium , selenium , barium, zinc) in plastic made toys imported to Palestine.

2- To raise awareness to policy makers on the need of urgent national policy for the removal of heavy metals from children toys in the Palestinian territories.

Chapter Two

Overview of Some Restrictions and Some Major Toys' Safety Standards

2. Overview of some restrictions and some major toys safety standards

2.1 Some International Toys' Safety Standards

The international community has issued a series of safety standards to restrict and control the use of heavy metals in toys. Table 2.1 below includes the standards of UN, EU, US, , China, Australia, Canada, Japan, Brazil, New Zealand ,Hong Kong, Jamaica ,Singapore, Malaysia.

Table 2.1 Toys safety standards of United Nations and other important industrial countries. Source (CPSC, 2011).

Region	Some Standard(s) and Regulations
International **UN**	ISO 8124-1:2000 Safety aspects relating to mechanical and physical properties ISO 8124-2: 1994 Flammability ISO 8124-3: 1997 Migration of certain elements ISO 8098: 1989 Cycles – safety requirements for bicycles for young children
Australia	AS/NZS ISO 8124.1-2002 Safety of toys (safety requirements) Part 1: Mechanical and physical property requirements AS/NZS ISO 8124 2-2003 Safety of toys (safety requirements) Part 2: Flammability requirements
Brazil	ABNT (Brazilian Association of Technical Standards) NBR 11786/1998 - Toy Safety
Canada	Technical Standards Safety Act and Upholstered and Stuffed Articles Regulation Hazardous Products Act R.S. c. H-3 Hazardous Products (Toys) Regulations C.R.C., c. 931 Regulations Respecting the Advertising, Sale and Importation of Hazardous Products (Pacifiers) under Hazardous Products Act
China	ISO 8124.1:2002 Safety of Toys - Safety aspects related to mechanical and physical properties GB 9832-93 Safety and Quality of Sewn, Plush and Cloth Toys GB 5296.5-96
European Union [6]	EN 71-1:2011 Safety of toys - Part 1: Mechanical and physical properties EN 71-2:2011 Safety of toys - Part 2: Flammability

	EN 71-3:2013 Safety of toys - Part 3: Migration of certain elements EN 71-4:2013 Safety of toys - Part 4: Experimental sets for chemistry and related activities EN 71-5:2013 Safety of toys - Part 5: Chemical toys (sets) other than experimental sets EN 71-8:2011 Safety of toys - Part 8: Activity toys for domestic us
Hong Kong	Toys and Children's Products Safety Regulation (in compliance with ASTM F963, or EN-71)
Jamaica	JS 90:1983 Jamaican Standard Specification for Safety of toys and playthings
Japan	The Japan Toy Association Toy Safety Standard Part 1 - Mechanical and Physical Properties Part 2 - Flammability Part 3 - Chemical Properties
Malaysia	Safety of Toys MS EN71 Part 1:1995 (P) Mechanical and Physical Properties MS ISO 8124-2:1999 Flammability MS EN71 Part 3: 1998 Migration of Certain Elements
Mexico	NOM 015/10-SCFI/SSA-1994 Toy Safety and Commercial Information - Toy and School Material Safety. Limits on the Bioavailability of Metals used on Articles with Paints and Dyes. Chemical Specifications and Test Methods.
New Zealand	AS/NZS ISO 8124.1:2002 Safety of Toys - Safety aspects related to mechanical and physical properties (ISO 8124.1:2000, MOD) AS/NZS ISO 8124.2:2003 Safety of Toys - Flammability (ISO 8124.2: 1994, MOD) AS/NZS ISO 8124.3:2003 Safety of toys - Migration of certain elements
Singapore	Safety of Toys: SS 474 PT. 1:2000 Part 1: Mechanical and Physical Properties SS 474 PT. 2: 2000 Part 2: Flammability SS 474 PT. 3: 2000 Part 3: Migration of Certain Elements
United States	*Mandatory Toy Safety Standard:* Code of Federal Regulations, Commercial Practices 16, Part 1000 to End (16CFR) U.S. Consumer Product Safety Commission Engineering Test Manual for Rattles U.S. Consumer Product Safety Commission Engineering Test Manual for Pacifiers U.S. Consumer Product Safety Commission Labeling Requirements for Art Materials Presenting Chronic Hazards (LHAMA) U.S. Child Safety Protection Act, Small Parts Hazard Warning Rule and Rules for Reporting Choking Incidents (September 2002) ASTM F963-07 Standard Consumer Safety Specification on Toy Safety (effective February 2009) ASTM F963-08 Standard Consumer Safety Specification on Toy Safety

The laws and acts are not fixed but they are changed and modified from time to time. The purpose of these changes and new regulations at the end is to ensure toy safety and to protect human health and the environment.

For example, the Consumer Affairs Ministry of Australia has declared a new toy safety standard that limits the use of lead and heavy metals in children's toys. This new safety standard had come into effect on January 1st, 2010 and had replaced the old Trade Practices Act ban on lead in toys, which was implemented in 2007 (Australian Competition & Consumer Commission,2008).

On May 11, 2009, European Union adopted the new toys directive, 2009/48/EC, which had come into force in member states on July 20, 2011. Compared with the old directive 88/378/EC, new 2009/48/EC has undergone substantial revisions in the aspects of chemical safety, physical mechanics, electric performance, sanitary safety and label requirement, etc. (CPSC,2011).The major changes are listed as below:

The new directive explicitly specifies that toys should not contain any carcinogenic, mutagenic substance or substances toxic to reproduction (CMR);

EN 71-3: EN 71-3 sets the highest limits of migrated elements (e.g. antimony, arsenic, barium, cadmium, chromium, lead, mercury and tin) in accessible materials or parts of toys. Migrated elements refer to the extracted solutes out of toy materials after a continuous contact with gastric acid.

EN 71-9: EN71-9 specifies the basic requirements for organic compounds in toys etc…..

At present, the requirements for maximum migration of eight heavy metals from toy materials are virtually identical in the US, Europe and in the ISO standards. They will, however, be changed in the near future.

The U.S. Consumer Product Safety Commission called on the toy industry to voluntarily stop making vinyl chewing toys that contain phthalates, (Thornton, 2000).

Total metal content and total migration limit

We must differentiate between two important concepts in this area. The first one is Total Heavy Metal Content, and the second is Maximum Soluble Migrated Element of toy material. But because most of the selected heavy metals elements in many studies such as (Justin Pritchard, study,2010), until recently have no strict standards or regulations in children's toys "Cadmium represents a stark example of this" most states adopted Maximum Soluble Migrated Element standards in assessment of heavy metals levels in plastic toys (ISO 8124-3:1997, Migration of Certain Elements). The material is placed under conditions which simulate contact with stomach acid for a period of time after swallowing. This method will be adopted in the current study. Tables (2.2), (2.3), (2.4) and (2.5) below show some International Maximum Soluble Migrated Element Standard.

UN Standard

Table 2.2 Maximum Soluble Migrated Element in ppm (mg/kg) Toy Material according to 1. ISO 8124 part 3: 1997 Migration of Certain Elements

Lead Pb	Cadmium Cd	Chromium Cr	Arsenic As	Mercury Hg	Selenium Se	Antimony Sb	Barium Ba
90	**75**	**60**	**25**	**60**	**500**	**60**	**1000**

USA Standards

Table 2.3 Maximum Soluble Migrated Element in ppm (mg/kg) Toy Material according to ASTM F963-08 4.3.5 The American Society of Testing and Materials (ASTM)

Lead Pb	Cadmium Cd	Chromium Cr	Arsenic As	Mercury Hg	Selenium Se	Antimony Sb	Barium Ba
90	**75**	**60**	**25**	**60**	**500**	**60**	**1000**

EU Standards

Table 2.4 Maximum Soluble Migrated Element in ppm (mg/kg) Toy Material (except modeling clay and finger paint) according to EN 71 part 3: 1994 and Amendment A1:2000+ AC:2002 Migration of Certain Elements Directive.

Lead Pb	Cadmium Cd	Chromium Cr	Arsenic As	Mercury Hg	Selenium Se	Antimony Sb	Barium Ba
90	**75**	**60**	**25**	**60**	**500**	**60**	**1000**

Canadian Standard

Table 2.5 Maximum Element in ppm (mg/kg) Surface Coating Materials. Canadian Hazardous Products Act, CHAPTER H-3(Version 2010) Schedule I Part I, Section 9 and Canada Surface Coating Materials Regulations (SOR/2005-109) with its amendment

Lead Pb	Cadmium Cd	Chromium Cr	Arsenic As	Mercury Hg	Selenium Se	Antimony Sb	Barium Ba
90	**1000**	**60**	**1000**	**10**	**1000**	**1000**	**1000**

What about zinc standards? According to EN 71-3: 1994, the maximum migration allowable limit of zinc in toy (mg/kg toy material) can be calculated from the following relation;

[Element in toy (mg/kg toy material) x weight of toy material (kg)/ Body weight child (kg)] must <10% of TDL, were TDI =Tolerable Daily Intake and it is for zinc 350 (µg/kg bw/day**)**. (SCF, 2003b), **(**RIVM, 2008).

Accordingly, The limit of element in toy (mg/kg toy material) =

10% TDI x Body weight child (kg)/ weight of toy material present in toy (kg)

The following exposure scenario and assumption are proposed:

Toys intended to be put in the mouth for children aged over 3 years

Body weight: 15 kg (based on 3-4 years of age)

Duration: 1 hour/day (worst case estimation)

Amount ingested: 8 mg/day

Absorption: 100% over the intestinal tract of the amount of element migrated out of the toy

2.2 Palestinian Standards

According to the Paris Protocol, the Palestinian specifications must match that of Israel regarding imported products except those that fall under A1 & A2 lists. But it must be noted that:

1. Most of the products imported under the afore mentioned A1 & A2 lists are imported to the PA area without performing any testing procedures (Chapter No. 12 in the book of customs procedures (Foreign Trade) issued by the Israeli Tax Authority, 2000).

2. The Palestinian Standard Institute (PSI) developed the needed technical specifications for only a limited number of imported products.

3. PSI has no role when the imported products' specifications meet the Israeli specification and these products enter the Palestinian area without the control of the Palestinian side. (Chapter No. 12 in the book of customs procedures (Foreign Trade) issued by the Israeli Tax Authority)

4.The inability of the PSI to test some imported goods due to the unavailability of proper laboratories and the necessary testing equipment; leading the Palestinian testing authority to use the available laboratories in neighboring countries such as Jordan.(National Economic Dialogue program)

5. In most cases a settlement is reached between the importer and the customs department as a lump sum amount paid by the importer (National Economic Dialogue program, 2008).

Goods often enter without restrictions or controls, standards or needs specially toys and plastics from China and scientifically proven the presence of cancer-causing precancerous Pale (Abul Khair. Mustafa Ahmed, 2007).

In the investigation by: Abdul Ghani Salamh "Does Palestinian consumer enjoyed any kind of protection?" 11/2/2012, Eng Omar Kabha, Director of Consumer Protection at the Ministry of Economy confirmed that, the examination does not include all sectors, for example there are important sectors cannot be covered due to Potential shortage, lack of specialized laboratories, and sometimes to their need for inspectors specialists, or because there is no Palestinian specification, these sectors include : toys, house wares, electrical and electronic appliances, automobiles and spare parts, construction materials .. Etc., and these and other issues are not absent from our thinking, but we made the subject of food a top priority, and thinking based on that cover the rest of the other sectors in the future, but when conditions improve and required capabilities are available.

The absence of the executive power of the follow-up field and the control and supervision: where the role of the authorities concerned on the subject is absent in one way or another, make a lot of goods such as toys enter the Palestinian cities like Hebron whether it be in the terminal itself, or in the many other outlets located in the vicinity of the city from all directions (Mr. Mustafa Ahmed Abul Khair, 2007).

Accordingly, in brief, Palestinian Authority has no authority over the ports and has limited authority over the crossings. The Israeli side is the one who does all these tasks and monitor the movement of goods coming from overseas, and examines their brands and their conformity with international standards.

The problem lies in that, there is no official Palestinian presence in Israeli ports, the handled occurs directly between the Palestinian merchant and the port authority and no one can be sure that Palestinian goods have been examined or not. In the end, as the goods will not go back inside Israel and will not hurt the Israeli citizen, Israel is not worried and Palestinian merchant - the weakest link here- wants the proportion of profit first and foremost. Israel collected the tax for the Palestinian Authority and the Palestinian citizen is the victim.

Whatever it, and whether the Palestinian Authority is responsible or the Israeli government, there is a quantity of toys enters the territories of the Palestinian Authority does not meet international standards.

Chapter Three

Materials and Methods

3. Materials and methods

3.1 Reagents and apparatus

1) - Milli-Q water. Produced by Taylor Technologies.

2) – Pure concentrated Nitric acid HNO_3. Produced by El Dorado Chemical Company.

3) - Hydrochloric acid (concentrated), HCl. Produced by El Dorado Chemical Company.

4) - Hydrogen peroxide 30% H_2O_2.produced by Arkema worldwide bleaching & chemicals.

5) - Digestion Vessels - 250-mL.

6) - Drying ovens - able to maintain 30EC + 4EC.

7) - Filter paper - Whatman No. 41 or equivalent.

8) - Centrifuge and centrifuge tubes.

9) - Analytical balance - capable of accurate weighings to 0.0001 g.

10) - Funnel or equivalent.

11) - Graduated cylinder or equivalent volume measuring device.

12) - Volumetric Flasks - 100-mL.

13) -The Microwave Accelerated Reaction System (MARS 6) manufactured by Analytk Jena Company.

14)- Artificial Saliva(Methyle-p-hydroxybenzoate2.00g/1, Na carboxymethylecellulose 10g/1, $MgCl_2.6H_2O$ 0.059g/1,KCl 0.625g/1, $CaCl_2.2H_2O$ 0.166g/1,K_2HPO_4 0.804g/1, KH_2PO_4 0.32g/1, PH 6.75

15) - Inductively Coupled Plasma Mass Spectrometry or ICP-MS spectrophotometer manufactured by Agilent 7500 ICP-MS.

(ICP-MS means the use of high temperature 6000-7000 K plasma discharge to generate positively charged ions)

The following steps provide a brief overview of how the Agilent 7500 analyzes a sample (www.agilent.com/chem/icpms1-800-227-9770).

1 The sample solution is pumped into the inlet system where it is nebulized, forming a fine sample aerosol.

2 The aerosol is then carried into high temperature argon plasma which atomizes and ionizes the sample to produce a cloud of positively charged ions.

3 The sample ions are extracted from the plasma into a vacuum system containing a quadrupole analyzer or mass filter. The analyzer can scan the mass range very quickly allowing a multi-element analysis to be performed on the sample.

4 The ions are focused into the analyzer where they are separated by their mass- to- charge ratio (m/z).

5 The ion concentration of a specific mass- to- charge ratio is measured by an electron multiplier detector.

6 The count rate obtained for a particular ion is compared with a calibration plot to give the concentration for that element in the sample (for quantitative analysis) see figure (3.3) below

The Agilent Technologies 7500 Series ICP- MS (Agilent 7500) can measure trace elements as low as one part per trillion (ppt) and quickly scan more than 70 elements to determine the composition of an unknown sample with a MassHunter Workstation software automates the analysis and accurately interprets the resulting data. The ICP/MS instrument consists of an on-board peristaltic pump that controls the flow of sample solution into and waste (drain) out of the instrument, a nebulizer (Micro Mist nebulizer) that uses a stream of argon to disperse the sample, an ICP Argon plasma torch using Argon as plasma gas, auxiliary gas and nebulizer (carrier) gas, two pumps for evacuation, quadrupole mass analyzer with 0.8 amu resolution at 10% height, an octapole reaction system (ORS), and electron multiplier detector. The operating conditions are as follows: nebulizer gas (argon) flow rate: 0.9 L/min, auxiliary gas (argon) flow 0.3 L/min,

3.2 Sampling

Fifty toys were purchased from three major Palestinian cities (Hebron, Nablus and Ramallah), and 17 toys purchased from Israeli markets (west Jerusalem, Beit Safafa neighborhood). They were randomly selected from shops selling toys wholesale , retail and stalls , taking into account that they are plastic toys, popular, cheap and medium-priced and that are accessible to children from middle and low-income.

3.3 Toys' Description and Classification

All types of toys were purchased from the above mentioned specified locations of the three Palestinian cities. The toys were typically bright in color and are available in largely darker shades of red, yellow, purple, blue and green or a mix of these colors. Some of these toys were soft and easily squeezable while the others are not flexible enough. The main types of toys were replicas of guns, balls, fruits, animals, baby, dolls and cars. Some of them were replicas of attractive eatables objects such as banana, and apple etc…

The toy samples were first subjected to an indicative test for PVC using the Beilstein test. The Beilstein test is based on the principle that copper halides vaporize readily, giving-off a blue-green coloured flame owing to the presence of copper (Barbara et. al. 1992).

To perform this test, copper wire (18–20 gauge) inserted into a cork (which served as an insulated handle) was heated in a blue Bunsen burner. The hot wire was placed on an inconspicuous part of the plastic toy to be tested in order to melt some of the polymer onto the wire; then the wire was re-heated in the flame. A blue-green coloured flame, which persisted only a few seconds, indicated the presence of a halogen (excluding fluorine) and suggested that the polymer might be PVC (Barbara. 1992).

Every toy have been weighed, photographed , given a special number and description in terms of color and shape and the country of production as shown in table (3.1) below.

Table 3.1 Classification of toys from Palestinian markets

Toy Code	Weight in grams	description	Color	Country of production	PVC
T1	38.00	Lion	Yellow	China	Yes
T2	44.00	Water gun	Yellow+ orange	China	Yes
T3	63.00	Barbie doll	Gold+ brown	China	Yes
T4	322.0	Toy train	Red and black	China	Yes
T5	65.00	Necklace	Green and blue	China	Yes
T6	89.00	Bracelet	Gold and silver	China	Yes
T7	250.0	Beads gun	Black and grey	China	Yes
T8	300.0	Duck	Yellow	China	Yes
T9	147.0	Dinosaur	Grey and black	China	Yes
T10	28.00	Pendant heart	Yellow, Silver, Red	China	No
T11	328.0	Elephant	Green +Grey	China	Yes
T12	177.0	Police care	White+ Blue	Unknown	Yes
T13	216.0	Truck Car	Green+ Yellow	Unknown	Yes
T14	33.00	Banana	Yellow	Unknown	Yes
T15	119.0	Ambulance	Red+ White	China	Yes
T16	96.00	Dinosaur	Orange	China	Yes
T17	181.0	Giraffe	Brown	China	Yes
T18	68.00	Kitchen Tools	Silver+ Gold	China	Yes
T19	159.0	Lorry car	yellow +green	China	No
T20	55.60	Fish toy	Purple	China	No
T21	412.0	Truck Car	Green +blue	India	Yes
T22	115.0	Snack	Black+ White	China	Yes
T23	246.0	Ox	Orange	China	Yes
T24	213.2	Camel	Yellow light	China	Yes
T25	55.00	Apple	Red+ green	China	Yes
T26	36.50	Mobile	White+ Blue	China	Yes
T27	45.60	Plastic fish	Pink+ Yellow	China	Yes
T28	27.30	Mirror	Pink	China	Yes
T29	217.0	Basketball	deep Orange	China	Yes
T30	339.0	Football	White+ Yellow	China	Yes

Table 3.1 Continued

Toy Code	Weight in grams	description	Color	Country of production	PVC
T31	450.00	Ball filled oil	Blue	China	Yes
T32	66.30	Mirror	Green+ Yellow	China	Yes
T33	721.0	Painted house	Many colors	China	No
T34	4.000	Ring	Red	China	Yes
T35	2450	Balls cilia	Purple	China	Yes
T36	53.00	Mobile	White+ Yellow	China	Yes
T37	29.20	Telephone	Black	China	Yes
T38	399.0	Caterpillar	Deep yellow	China	Yes
T39	25.60	Pendant	Blue + green	China	Yes
T40	57.00	Dog	Grey	China	No
T41	69.00	Jelly ball	Blue	Unknown	No
T42	250.0	Soldiers	Green + Brown	Unknown	No
T43	217.0	Sword	White +Blue	Unknown	Yes
T44	119.5	Donkey	Brown	Unknown	Yes
T45	117.6	Zebra	Black + White	China	Yes
T46	5.000	Breastfed	Milky color + red	China	No
T47	135.0	Motorcycle	Grey and Blue	China	No
T48	248.0	Toy gun	Black	China	No
T49	39.00	Flower	Red	China	Yes
T50	75.50	Cat	Grey	China	Yes

The photos of the samples are shown in Appendix B

Table 3.2 Classification of toys from the Israeli market

Toy Code	Weight in grams	description	Color	Country of production	PVC
S1	195	Duck	Yellow	China	Yes
S2	313	Lorry Car	Green	China	Yes
S3	178	Ox	Orange	China	Yes
S4	288	Caterpillar	Deep Yellow	China	Yes
S5	207	Toy Gun	Black	China	Yes
S6	450	JCP tractor	Yellow	China	Yes
S7	66.3	Mobile	Green +Yellow	China	Yes
S8	721	Cottage	Many colors	China	No
S9	14	Cup	Red	China	Yes
S10	245	Balls cilia	Many colors	China	Yes
S11	53	Lego	Many colors	China	Yes
S12	29.2	Telephone	Black	China	Yes
S13	397.7	Motorcycle	Grey +Blue	China	Yes
S14	25.6	Barbie Toy	Brown	China	Yes
S15	58.5	Dog	Brown	China	No
S16	69	Plane	Green + Yellow	Unknown	No
S17	250	Tractor	Green + Yellow	Unknown	No

Refer to Appendix B to see the photos of the samples

All toys were further grinded crushed, sieved through < 2 mm nylon sieve, and mixed as necessary to homogenize the samples.

Figure 3.1 a sample of toys crushed, grinded, and sieved uniformly

The samples were stored in closed cans and each sample was given a unique number similar to the number carried by its original toy. Samples were digested in AL-Quds laboratory in order to dissolve and completely liberate the metals from the polymeric matrices. The solution was analyzed by laboratory methods (ICPMS in this study) to determine the concentrations of metals in these samples.

There are many well known methods to carry out the digestion process, such as EPA SW-846 which includes (Method 3050B, Method 3051A, Method 3052), and Method CPSC-CH-E1002-08 (Kingston and Walter, 1992). But we compared them and have chosen the best suitable for the current study. We have found after careful comparison and looking at the competence, the positives and negatives of each method that the best method was EPA3052 (Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices), because it is appropriately used to determine the total concentration of heavy metals such as cadmium, lead, chromium, selenium, mercury…etc in flexible and non flexible PVC, since PVC is an organic material (Kingston and Walter, 1992).

The absolute total digestion was required in our study case. If the sample is not completely digested, the heavy metals are not sufficiently liberated from the plastic and cannot be completely measured by the laboratory analytical equipment, since analytical instruments, such as ICP, measure the concentration of substances in the solution and not in the solid as mentioned above (Kingston and Walter, 1992).

The EPA3052 Acid Digestion method involved the following steps: (Kingston and Haswell, 1997). All chemicals used were ultra pure grade.

1) - All digestion vessels and volumetric instruments were carefully acid washed and rinsed with reagent water. This cleaning procedure has been used whenever the prior use of the digestion vessels is unknown or cross contamination from vessels is suspected.

2) -The Microwave vessels were weighed before and after digestion to evaluate seal integrity and for more accuracy.

3) - A well-mixed samples were weighed and placed into microwave vessels (The samples weights ranged between 0.01 to 0.2 g).

4) - About 10ml of concentrated nitric acid was added to the vessel in a fume hood, followed by 2ml of hydrogen peroxide (30%) in order to get complete oxidation of organic matter. Five ml of milli-Q water were also added to improve the solubility of minerals and prevent temperature spikes due to exothermic reactions.

5) - The vessels were sealed, properly placed in the microwave system according to the manufacturer's recommended specifications, temperature and pressure sensors were connected appropriately to vessels according to manufacturer’s specifications, Figure (3.2).

Figure 3.2 Sealed vessels in The Microwave Accelerated Reaction System (MARS5)

6) - The temperature of each sample reached 180 ± 5 ºC in approximately 5.5 minutes and remained at this temperature for 10 minutes. The pressure reached the peak at the eighth minute ± 3 for most of the samples. The pressure was reduced in some cases, by the relief mechanism of the vessel, because it exceeded the pressure limits of the vessel.

7) - At the end of the microwave program, the vessels was allowed to cool for a minimum of 10 minutes before removing them from the microwave system. The microwave vessels remained closed throughout the digestion process.

8) - All the vessels were carefully uncapped and vented in a fume hood.

9) – The vessel contents or digestible obtained were then filtered through a 0.41 μm membrane filter, diluted to total volume 50 ml with deionized water DI and transferred for ICPMS analysis.

All of these samples have been analyzed for (Pb, Cd, Cr, Hg, As, Se, Ba, and Zn) using Agilent 7500 ICPMS in the aquatic environmental laboratory in Al-Quds University.

Figure 3.3 Agilent 7500a Inductively Coupled Plasma Mass Spectrometer

3.4 Heavy metals migration rates experiment

Ten toy samples (2.5gm each) have been crushed and dipped for 8 hours in a solution of artificial saliva (20ml) with specifications mentioned above. The artificial saliva was acidified and tested for heavy metal concentrations.

Chapter Four

Results and Discussion

4.1 Results

The results of heavy metals concentrations in the toy samples are presented in ppm in Table 4.1 for PVC Toys and in table 4.2 for non PVC Toys. The Data in Table (4.3) represents heavy metal concentrations of Israeli samples in ppm.

Table 4.1 Concentrations of eight heavy metals in PVC and non PVC made toys in mg/kg or in ppm

Sample code	Pb	Cd	Cr	Hg	AS	Se	Ba	Zn
T1	1775.70	2.05	471.37	<DL	471.37	1778.0	167.70	3377.00
T2	2.65	113.40	1858.16	<DL	1858.16	1080.70	104.50	7526.80
T3	22.56	139.40	511.60	<DL	511.60	1292.0	108.50	3443.90
T4	19.89	1.80	56..30	<DL	44.09	454.050	26.70	1337.00
T5	58.80	<DL	524.20	<DL	542.09	70.65	27.00	1075.27
T6	0.76	251.69	220.40	<DL	220.40	868.20	40.06	10725.00
T7	31.94	0.49	2468.50	<DL	2486.50	143.20	45.50	487.00
T8	48.98	0.49	50.77	<DL	4.28	237.40	199.40	193.39
T9	1431.00	27.00	22.43	<DL	39.80	105.33	222.70	1560.00
T10	18.92	2.70	12.93	<DL	7.34	100.86	16074.40	3875.80
T11	611.96	<DL	105.20	<DL	105.20	150.00	116.07	1933.90
T12	18.92	11.53	129.00	<DL	7.76	259.20	5768.00	226.20
T13	55.50	324.50	11.32	<DL	10.00	105.80	6.77	3875.80
T14	5467.00	4.21	182.00	<DL	4.30	147.90	7.00	<DL
T15	1886.64	47.50	19.30	0.12	42.88	169.25	5530.70	158.26
T16	5467.78	436.42	295.60	47.20	2.90	291.40	3403.60	2119.80
T17	18.87	1.25	50.73	12.18	57.17	363.80	100.50	776.00
T18	77.80	18.10	33.20	1.05	15.40	56.63	33.13	114.00
T19	6036.00	193.78	16. 27	4.70	14.72	463.00	19.30	2110.40
T20	45.65	289.60	91.11	2.70	16.06	773.77	25.40	1000.00
T21	661.76	0.73	203.45	2.70	203.45	508.00	30.14	2017.00
T22	109.85	19.39	40.19	3.10	18.80	1700.40	73.89	188.80
T23	2919.69	28..59	66.10	0.80	66.70	884.40	<DL	582.20
T24	1405.00	26.88	32.48	<DL	16.00	88.20	24.13	888.15

T25	45.65	40.50	117.15	0.5	117.50	104.06	57.90	1110.40
T26	66.17	63.93	16.265	6.45	39.15	79.29	125.24	171.70
T27	9.58	7.08	81.12	5.2	6.67	431.81	80.80	65.44
T28	29.20	22.23	11.56	35.22	111.56	441.50	83.97	191.50
T29	2044.70	100.50	14.025	85.90	43.80	980.00	2550.00	139.00
T30	177.15	46.50	51.06	<DL	<DL	16.06	48.50	37.00
T31	397.30	≤DL	28.2.5	<DL	11.16	1000.81	49.90	73.76
T32	79.80	10.05	359.87	0.48	4.30	530.00	70.70	37.76
T33	1021.60	4.48	17.315	<DL	5.83	16.22	35.76	45.45
T34	975.50	10.40	191.6	<DL	191.60	299.10	202.50	300.0
T35	87.45	3.34	89.30	<DL	89.30	53.85	2066.50	<DL
T36	48.45	24.46	89.15	<DL	<DL	120.60	9159.00	9.20
T37	1021.60	0.47	53.513	<DL	49.90	24.24	5606.00	16.29
T38	8195.60	<Dl	194.00	6.60	48.00	553.00	134.60	<DL
T39	1761.00	<DL	<DL	<DL	8.92	227.00	5654.30	<DL
T40	40.00	256.35	11.94	6.4	4.99	65.80	1670.04	24.70
T41	84.01	420.00	<DL	<DL	4.80	693.00	351.00	4618.00
T42	8195.00	150.18	44.02	8.59	<DL	77.27	181.80	1000.00
T43	1761.00	49.50	15.6	63.6	<DL	2833.00	88.96	166.42
T44	29.03	25.37	52.22	18.6	<DL	108.76	104.62	638.00
T45	47.90	298.66	11.824	64.60	18.80	112.77	1325.90	3789.0
T46	<DL	349.44	56.00	<DL	19.20	151.90	55.24	588.60
T47	10.05	90.43	56.00	<DL	19.20	19.20	94.52	875.00
T48	27.70	9.51	6.76	6.9	<DL	449.80	50.00	1369.00
T49	10.05	29.87	48.20	2.55	<DL	599.30	<DL	905.99
T50	26.45	34.94	349.44	1.6	<DL	618.40	<DL	1157.00

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*Red values in the preceding 4-1 table represent the concentrations of heavy metals that exceeded the allowable limit internationally

*The calibration curves for the standards that were used for measuring these values are illustrated in Appendix (A).

*ND = Not detected, < D = below detection li

The percentages of Palestinian toys samples that have heavy metals total content that exceeded the maximum allowable limits are shown in Figure 4.1below.

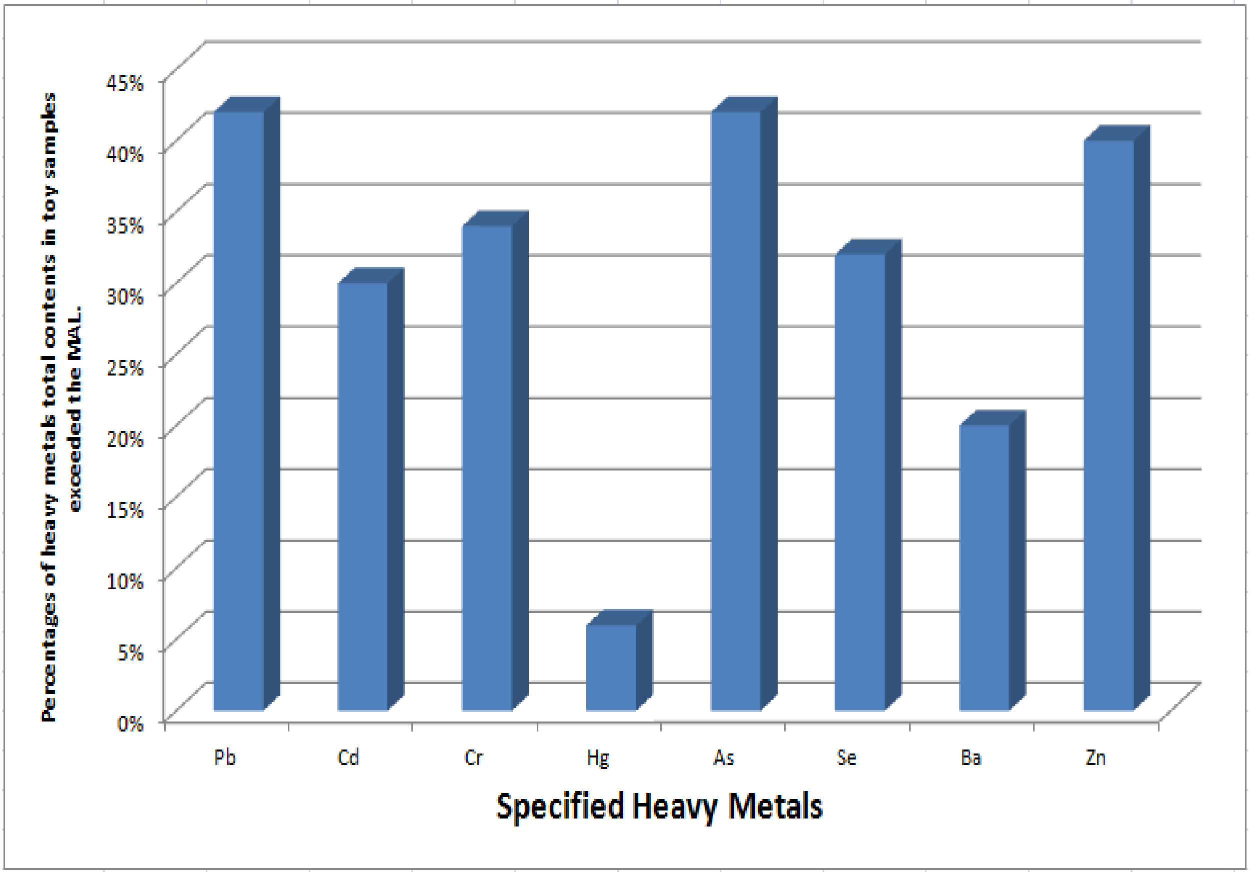

Figure 4.1 percentages of toys samples from Palestinian market that contain heavy metals total content exceeding the maximum allowable limits

Table 4.2 Concentrations of eight heavy metals in non PVC made toys in ppm ($mgkg^{-1}$)

Sample Code	Pb	Cd	Cr	Hg	AS	Se	Ba	Zn
T10	18.92	2.7	12.93	<DL	7.34	100.86	16074.40	3875.80
T19	6036.00	193.78	16. 2.6	4.70	14.72	463.00	19.30	2110.40
T20	45.65	289.60	91.11	2.70	16.06	773.77	25.40	1000.00
T33	1021.60	4.480	17.36	<DL	5.86	16.22	35.76	45.45
T40	40.00	256.35	11.94	6.40	4.99	65.80	1670.04	24.70
T41	84.01	420.00	<DL	<DL	4.80	693.00	351.00	4618.00
T42	8195.00	150.18	44.02	8.59	<DL	77.27	181.80	1000.00
T46	<DL	349.44	56.00	<DL	19.20	151.90	55.24	588.60
T47	10.05	90.43	56.00	<DL	19.20	19.20	94.52	875.00
T48	27.70	9.51	6.76	6.90	<DL	449.80	50.00	1369.00

Table 4.3 concentrations of eight heavy metals in Seventeenth toy samples from Israeli market

Sample Code	Description	Color	Pb	Cd	Cr	Hg	As	SE	Ba	Zn
S1	Duck	Yellow	73.0	51.5	49.3	25.0	16.0	342.0	411.5	96.00
S2	Lorry Car	Green	18.0	69.0	57.0	11.8	21.9	219.0	253.0	473.00
S3	Ox	Orange	86.2	66.7	59.0	6.3	13.0	99.7	456.0	316.00
S4	Caterpillar	Deep Yellow	75.0	71.2	44.3	15.3	22.2	217.3	489.0	488.00
S5	Toy Gun	Black	14.0	33.0	58.0	3.2	11.2	99.8	218.2	500.00
S6	JCP tractor	Yellow	95.2	75.2	61.0	ND	ND	38.5	95.0	111.40
S7	Mobile	Green +Yellow	41.2	27.6	43.8	ND	ND	17.5	113.1	<DL
S8	House	Many colors	37.8	41.2	39.0	ND	ND	54.3	83.9	92.00
S9	Cup	Red	13.2	5.60	<DL	ND	ND	0.71	15.6	25.30
S10	Balls cilia	Purple	23.1	14.7	11.5	ND	ND	18.3	24.2	16.00
S11	Lego	Many colors	2.80	4.50	11.9	ND	ND	0.98	35.4	71.00
S12	Telephone	Black	28.4	18.6	24.1	ND	ND	84.0	117.0	58.00
S13	motorcycle	Grey +Blue	84.3	77.2	57.6	ND	ND	214.0	154.0	66.90
S14	Barbie Toy	Brown	11.0	9.30	14.8	ND	ND	29.00	41.20	110.00
S15	Dog	Brown	6.94	8.36	7.15	ND	ND	42.00	63.00	102.00
S16	Plane	Green +Yellow	9.54	12.8	10.1	ND	ND	75.30	14.00	114.00
S17	Tractor	Green + Yellow	39.7	42	78.3	ND	ND	44.00	72.30	88.90

*ND = Not detected

*< D = below detection limit

4.2 Heavy metal concentrations in the toy samples from Palestinian market and their interpretation.

Lead

The concentration of lead was found to range from (0.76 to 8195.6 ppm) with an average of 464.48 ppm. Forty two percent of the toy samples (twenty one out of 50 toys samples), contain lead with concentration higher than 90 ppm, (Table 4.4). The lead limit according to U.S. Environment Protection Agency (EPA) Standards (40 CFR Part 745, 2001) for toys and other articles intended for use by children is 90ppm.

The average value for the concentration of lead that was found in this study (464.48 ppm) is much more than the maximum allowable value of 90 ppm.

Also the study revealed that there is a close correlation between the color of the sample and the concentration of heavy metal, for example, samples of yellow, orange and green colors contain a high concentration of lead. Most of the yellow samples contain the highest concentration of lead. This may be attributed because lead and its compounds are used as pigments (Van Alphen M 1999; Clark et.al, 2006). Lead (II) chromate (PbCrO4, "chrome yellow") is used to produce yellow, orange, red green paints color. Lead (II) carbonates (PbCO3, "white lead") to produce white color. Red lead (lead oxide with 4 oxygen's Pb_3O_4) to produce red and bright orange color. Blue lead (lead sulfate with lead oxide, zinc oxide, and carbon) may be used industrially as a corrosion protection and as a color when metal is needed (US CDC, 2007).

So the highest lead concentration in toy samples of most yellowish color is due mainly to Lead (II) chromate ($PbCrO_4$).

Lead was present in different concentrations in most tested samples, but the percentage of concentration in samples made from PVC polymer was higher than in samples made from other polymers. This maybe because PVC has a brittle nature and heat sensitivity, so it requires the use of a thermal stabilizers to enhance (reinforce) material properties, reduce material costs (fillers) and impart specific characteristics such as stability against heat and light, flexibility, flame resistance, or provide color and aesthetics, etc, (Greenpeace, 2008).

The commonly used stabilizers are usually basic lead salts that can react with the evolved hydrogen chloride gas, thus they retard the deleterious catalytic action of the eliminated hydrogen chloride, or substances that can exchange the labile functional group in the backbone chain for other more stable substituent derived from the stabilizer (Titow, 1985). (US EPA, 2003).

Table 4.4 PVC toy samples with lead concentration >90 ppm (mg/kg)

Description	Lead	Color
T1 (Lion)	1775.70	Yellow
T9 (Dinosaur)	1431.00	Green + Yellow
T11 (Elephant)	611.96	Green +Grey
T14 (Banana)	5467.00	Yellow
T15 (Ambulance)	1886.64	Red + White
T16 (Dinosaur)	5467.78	Orange
T19 (Lorry car)	6036.00	Yellow + Green
T21 (Truck Car)	661.76	Green +Blue
T22 (snack)	109.85	Black + White
T23 (Ox)	2919.69	Orange
T24 (Camel)	1405.00	Yellow Light
T29 (Mirror)	2044.70	Pink
T30 (football)	177.15	White + Yellow
T31 (Ball filled oil)	397.30	Blue
T33 (Painted house	1021.60	Many Colors
T34(Plastic Ring)	975.50	Red
T37 (Telephone)	1021.60	Black
T38 (Caterpillar)	8195.60	Deep Yellow
T39 (Pendant)	1761.00	Blue+ green
T42 (Soldiers)	8195.00	Brown + Green
T43 (Sword)	1761.00	Blue + White

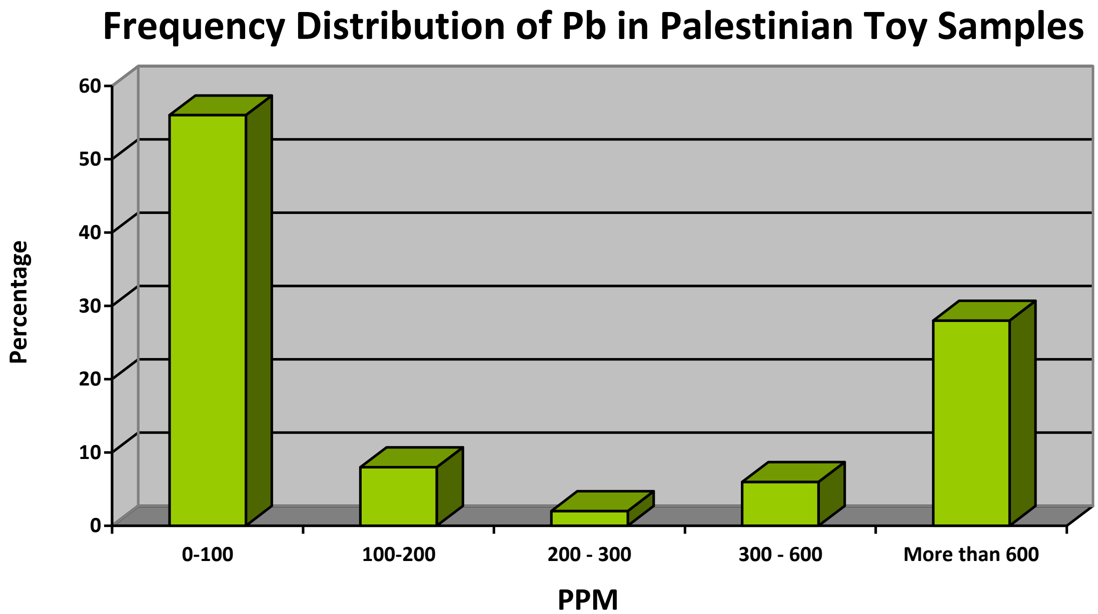

Figure 4.2 Frequency of Pb in Palestinian Toy samples

Cadmium

The results of Cadmium metal concentration are shown in Table 4.5 Twenty eight percent of the samples (Fourteenth samples out of 50) contain cadmium concentration of more than 75 ppm or mg/kg. This means that 28% of the samples have high cadmium concentration above the maximum allowable value. Cadmium concentrations were ranging from 0.47 to 436.42 ppm (mg/kg) with an average of 125.9 ppm.

Some of the toy samples were found to contain very high concentrations of Cadmium. These values exceeded the limit of what is permissible internationally.

Cadmium is used as a thermal stabilizer for polyvinyl chloride (PVC) plastic during the manufacturing process. (O. M. Folarin and E. R. Sadiku,2011). Its function can be summarized as “It replaces labile chlorine atoms in the polymer and modify chain reactions. It inhibits the elimination of hydrogen chloride and interrupt the formation of polyene sequences in the polymer" which is attributed to its formation of the gradually demise of yellow and its conversion to orange and then red and brown. (Folarin O. M. and Sadiku E. R.).

Cadmium is primarily used to color plastics, it is typically used to produce shades of yellow, orange, red, and maroon but it is also used in pigments for ceramics, glass, textiles, printing, inks, rubber, lacquers, and specialty paints (US EPA, 2000).
Some of these items are used in one way or another in plastic toys. High Cadmium concentrations were noted in deep orange toy samples.

Table 4.5 Samples of PVC and non PVC toys with cadmium concentration > 75mg/kg (the maximum allowable limit)

Description	Cadmium	PVC	Color
T2 (Water gun)	113.40	Yes	Yellow + Orange
T3 (Barbie doll)	139.14	Yes	Gold + Brown
T6 (Bracelet)	251.69	Yes	Gold + Silver
T13 (Truck car)	324.50	Yes	Green
T16 (Dinosaur)	436.42	No	Orange
T19 (Lorry car)	193.78	No	Yellow + Green
T20 (Fish)	289.59	Yes	Purple
T29 (Basketball)	100.50	Yes	Deep Orange
T40 (Dog)	2563.50	No	Grey
T41 (Jelly ball)	420.00	No	Blue
T42 (Soldiers)	150.18	No	Green + Brown
T45 (Zebra)	298.66	Yes	White + Black
T46 (Breastfed)	349.44	No	Red + milky
T47 (motorcycle)	90.43	No	Grey + Blue

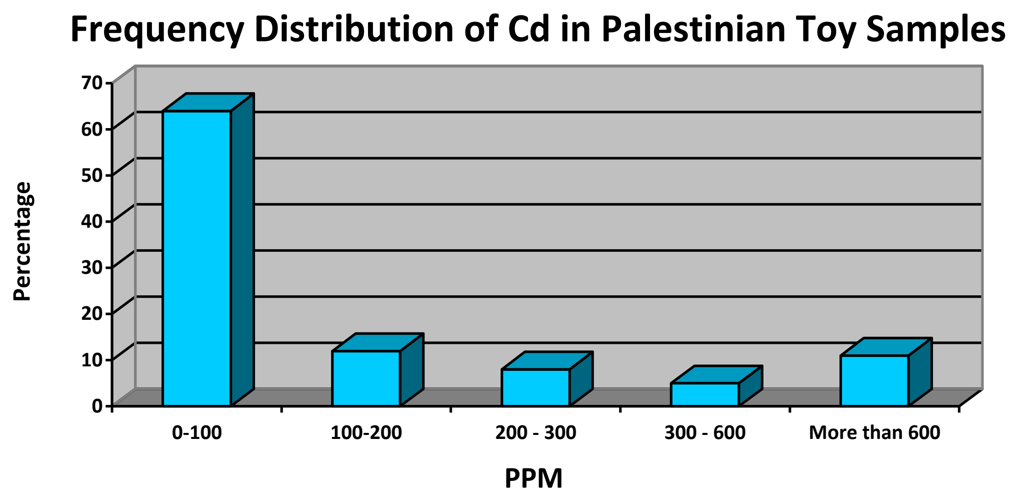

Figure 4.3 Frequency of Cd in Palestinian Toy samples

Mercury

The results of mercury metal concentration are shown in Table 4.6 Six percent of the samples (three samples out of 50) contain mercury concentration more than 60 ppm or mg/kg. This means that 6% of the samples have high mercury concentration above the allowable value. Mercury concentrations were varied from (0.118 to 85.9) ppm (mg/kg) with an average of 8.8 ppm .

Table 4.6 samples of PVC toys with mercury concentration > 60 mg/kg (the maximum allowable limit).

Description	**Mercury**	**Color**
T29 (Basketball)	85.9	Orange
T43 (Sword)	63.6	White + Blue
T45 (Zebra)	64.6	White + Black

Those three samples were made in china. Most manufacturers of PVC around the world use natural gas or petroleum as the feedstock or raw material from which the plastic is manufactured. However, most PVC manufacturing in China uses a different process that starts with coal as the feedstock. In that coal-based process, mercury is used as a catalyst to spark the chemical reaction among ingredients (UNEP, 2008)

In 2009, the coal-based process was used at 94 of 104 China's VCM (vinyl chloride monomer) plants. Although these plants accounted for only about 63% of China's PVC production, according to the latest data provided by their trade association (UNEP, 2008). Some of the mercury catalyst is lost during this industrial process and must be continually replenished. It is poorly understood exactly where the lost mercury ends up and how it gets there, but surely there is a part of it is mixed in processed material (UNEP, 2008). China's PVC manufacturing industry represents one of the most significant uses of mercury in the world today; it consumes over 800 metric tons per year (UNEP, 2008)

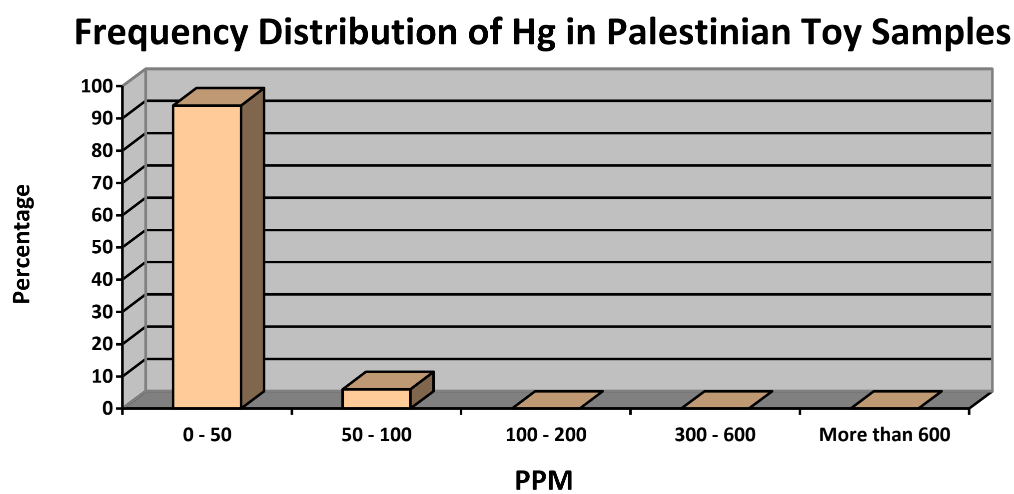

Figure 4.4 Frequency of Hg in Palestinian Toy samples

Chromium

The result of Chromium metal concentration is shown in Table 4.7 Thirty four percent of the samples (Seventeen samples out of 50) have Chromium concentration more than 60 ppm or mg/kg. This means that 34% of the samples contain high Chromium concentration and it is above the allowable value. Chromium concentrations were varied from 6.76 to 2468.0 ppm (mg/kg) with an average of 180.74 ppm.

Chromium is used widely as a valuable dye and as a coloring for PVC material, as well as heat stabilizer. Chromium is available in red color samples in the form of lead chromate molybdate sulfate red (formula $Pb(Cr,S,Mo)O_4$), In green color samples in the form of Chromium oxide Cr_2O_3 (This compound has the ability to reflect infrared light), in blue color samples in the form of Cobalt chromate, cobalt chromate, which, contains chromium in the matrix in addition to cobalt and aluminum. Empirical formula is $Co(Al,Cr)_2O_4$. It is also found in orange color samples in the form of chrome orange, which is a basic lead chromate formed under alkaline conditions to give product of empirical formula $PbCrO_4$. xPbO. Shades from a yellow-shade to a red-shade orange can be produced, depending on the alkalinity of the reaction mass. Yellow color samples in the form of Primrose chrome yellow, which it is a co precipitate of lead chromate and lead sulfate of empirical formula PbCrO4.$x$$PbSO_4$ and so on (Boscolo P, Gioacchino MD, Bavazzano P, White M, Sabbioni E, 1997).

The most important observation here was the strongest correlation between the presence of lead and the presence of chromium in the toy samples. The samples that have high lead concentration were often also containing chromium. This confirms that both of these two elements are used as dyes or pigments more than stabilizers and the compound combining them was lead chromate.

Table 4.7 PVC toy samples with chromium concentration >60 ppm (mg/kg)

Description	Chromium	Color
T1 (Lion)	471.37	Yellow
T2 (water gun)	1858.16	Orange + yellow
T3 (Barbie doll)	511.60	Gold + brown
T5 (Necklace)	524.20	Green + blue
T6 (Bracelet)	220.40	Silver + gold
T7 (Beads gun)	2486.50	Black + grey
T11 (Elephant)	105.20	Green + grey
T16 (Dinosaur)	295.60	Orange
T21 (Truck car)	203.45	Green + blue
T23 (Ox)	66.16	Orange
T25 (Apple)	117.15	Red + green
T28 (Mirror)	111.56	Pink
T32 (mirror)	359.87	Green + yellow
T34 (Ring)	191.60	Red
T35 (Ball cilia)	89.30	Purple
T36 (Mobile)	89.15	White + yellow
T38 (Caterpillar)	194.00	Deep yellow

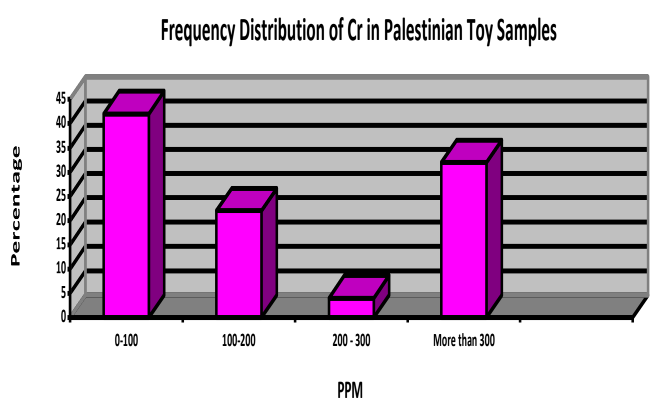

Figure 4.5 Frequency of Cr in Toy samples from Palestinian market

Barium

The results of Barium metal concentrations are shown in Table 4.8 Twenty percent of the samples (10samples out of 50) have Barium concentration more than 1000 ppm or mg/kg. This means that 20% of the samples have high cadmium concentration above the allowable value. Barium concentrations were ranged from 6.76 to16074 ppm (mg/kg) with an average of1240 ppm,

Barium is added to PVC polymer products including toys. Its compounds form the sources of white and yellow light in toys materials through the following barium compounds:

1. Natural barium sulfate, known as barite, has a high brightness, high specific gravity,and low oil absorption inert filler. It finds use in powder coatings of its high specific gravity, good brightness and low oil absorption (Dibello et.al. 2003).
2. Barium oxide which is responsible for white-yellow color.
3. Barium sulfide which responsible for grey color, and represents the starting point for the chemical manufacture of most other barium compounds (Dibello et.al. 2003). One such useful compounds is lithophone stone that consists of 28% zinc sulfide (ZnS) and 72% barium sulfate (BaSO4), which is used as a white pigment in paints coating plastic toys.

Table 4.8 Toys samples with barium concentration >1000 ppm (mg/kg)

Description	Barium	PVC	Color
T10 (Pendant heart)	16074.4	Yes	Yellow + Silver
T12 (Police care)	5768.0	Yes	White + Blue
T15 (Ambulance)	5530.7	Yes	Red + white
T16(Dinosaur)	3403.6	Yes	Orange
T29 (Basketball)	2550.0	Yes	Deep Orange
T35 (Balls cilia)	2066.5	Yes	Purple
T36 (Mobile)	9159.0	Yes	White + Yellow
T37 (Telephone)	5606.0	Yes	Black
T40 (Dog)	16074.0	No	Grey
T45 (Zebra)	1325.9	Yes	Black + White

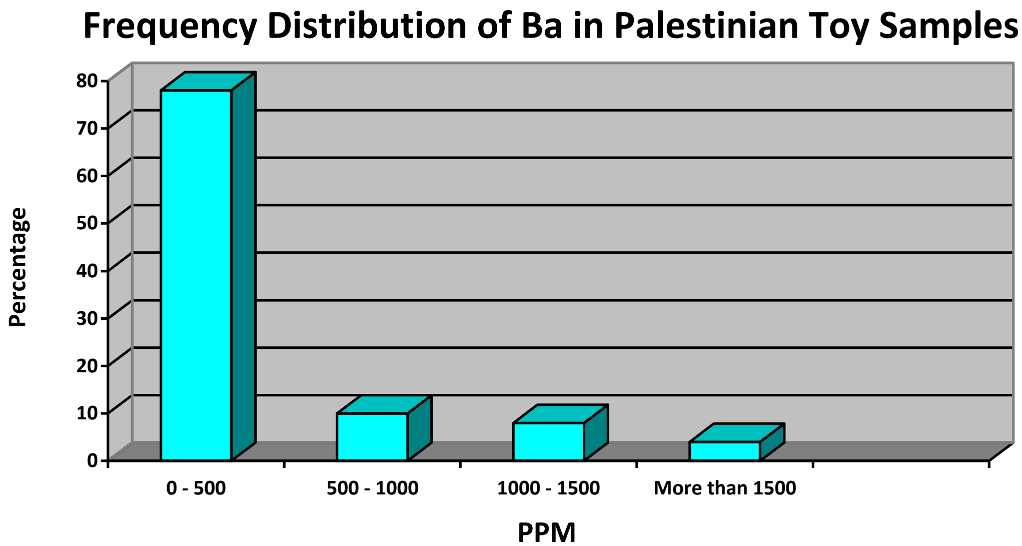

Figure 4.6 Frequency of Ba in Palestinian Toy samples

Zinc

The results of Zinc metal concentration is shown in Table 4.9. Forty percent of the samples (20 samples out of 50) have Zinc concentration more than 1000 ppm or mg/kg. This means that 40 % of the samples contain high zinc concentration above the maximum allowable value. Zinc concentrations were ranged from 9.5 to 10725.0 ppm (mg/kg) with an average of1361ppm.

Zinc is found in these toys in the form of zinc borate xZnO ·yB2O3· zH2O, x=4, y=1, z=1, which is widely used as a flame retardant. Zinc borates can either be used alone or in combination with other halogen synergists, such as antimony trioxide. In some instances Zinc borate is used with alumitrihydrate (Aluminium Trihydrate is an odorless powdery substance and it is a common primary ingredient present in most solid surface material and accounts for as much as 70% of the total product) to form a glass-like substance that inhibits polymer degradation. (Kirk, Othmer, 1970).

This thermal stability makes it attractive as a fire retardant additive for plastics, rubbers and PVC products that require high processing temperatures. It is also used as an anticorrosive pigment in coatings (C.Aykut ERDO_DU, 2004).

Zinc is also found in the form of ZINC OMADINE Zinc 2 -pyridinethiol -1-oxide, ($C_{10} H_8 N_2 O_2 S_2 Zn$), Mol. Wt. = 317.7, Melting pt. = 2400C (decomposes). It is used as antimicrobial agent in hair care products, in PVC and other plastics, in paints, coatings, adhesives, sealants, and as a cosmetic preservative are also available (Lilli Sherman, 2011).

Due to its low solubility in water (8 ppm at neutral pH), Its decomposition by ultraviolet light is slow, providing years of protection even against direct sunlight. Its antimicrobial effect is proposed to derive from its ability to disrupt membrane transport by blocking the proton pump that energizes the transport mechanism (Chandler, 1978).

Table 4.9 Toys samples with zinc concentration >1000 ppm

Description	Zinc	PVC	Color
T1(Lion)	3377.0	Yes	Yellow
T2(Water gun)	7526.8	Yes	Yellow + Orange
T3(Barbie doll)	3443.9	Yes	Gold+ Brown
T4(Toy train)	1337.0	Yes	Red +Black
T5(Necklace)	1075.3	Yes	Green+ blue
T6(Bracelet)	10725.0	Yes	Gold + Silver
T9(Dinosaur)	1560.0	Yes	Yellow
T10(Pendant heart)	3875.8	No	Silver+ blue + Red
T11(Elephant)	1933.9	Yes	Green +Grey
T13(Truck car)	3875.8	Yes	Green +Yellow
T16(Dinosaur)	2119.8	Yes	Orange
T19(Lorry car)	2110.4	No	Green +Yellow
T20(Fish toy)	1000.0	No	Purple
T21(Truck car)	2017.0	Yes	Green + Blue
T25(Apple)	1110.4	Yes	Red + Green
T41(Jelly ball)	4618.0	No	Blue
T42(Soldiers)	1000.0	No	Green + brown
T45(Zebra)	3789.0	Yes	Black + White
T48(Toy Gun)	1369.0	No	Black
T50(Flower)	1157.0	Yes	Red

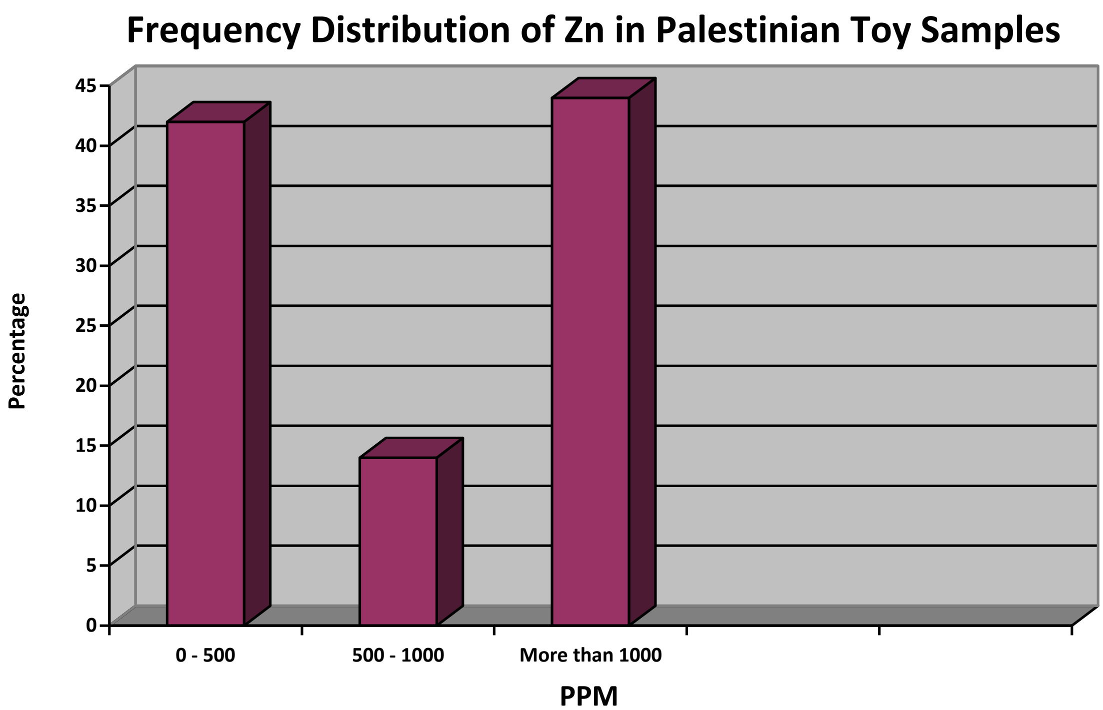

Figure 4.7 Frequency of Zn in Palestinian Toy samples

Selenium

The results of Selenium metal concentration is shown in Table 4.10. Thirty two percent of the samples (16 samples out of 50) contain selenium concentration more than 500 ppm or mg/kg. This means that 32% of the samples contain high selenium concentration above the allowable value. Selenium concentrations were ranging from 16.06 to 2833.0 ppm (mg/kg) with an average of 453.978 ppm,

Table 4.10 Toys samples with selenium concentration >500 ppm (mg/kg)

Description	Selenium	PVC	Color
T1 (Lion)	1778.0	Yes	Yellow
T2 (Water gun)	1080.0	Yes	Yellow + Orange
T3 (Barbie doll)	1292.0	Yes	Gold + Brown
T6 (Bracelet)	886.3	Yes	Gold + silver
T20 (Fish)	773.8	No	Purple
T21 (Truck car)	508.0	Yes	Green + Blue
T22 (Snack)	1700.0	Yes	Black + White
T23 (Ox)	884.4	Yes	Orange
T29 (Basketball)	980.0	Yes	Deep Orange
T31(Ball filled oil)	1000.8	Yes	Blue
T32 (Mirror)	530.0	Yes	Green + Yellow
T38 (Caterpillar)	553.0	Yes	Deep Yellow
T41 (Jelly ball)	693.0	No	Blue
T43(Sword)	2833.0	Yes	White + Blue
T49 (Flower)	599.3	Yes	Red
T50 (Cat)	618.4	Yes	Orange

Selenium is used as pigments (coloring agents) for paints, plastics, ceramics, and glazes* (Los Alamos National Laboratory, 2001) Depending on the form of selenium used; the color ranges from deep red to light orange. It can be used to decolorize glass and to impart a scarlet red color to glass, glazes and enamels.

Glazes* means: Something used to give a glossy surface or a coating of colored, opaque, or transparent material applied to ceramics before firing

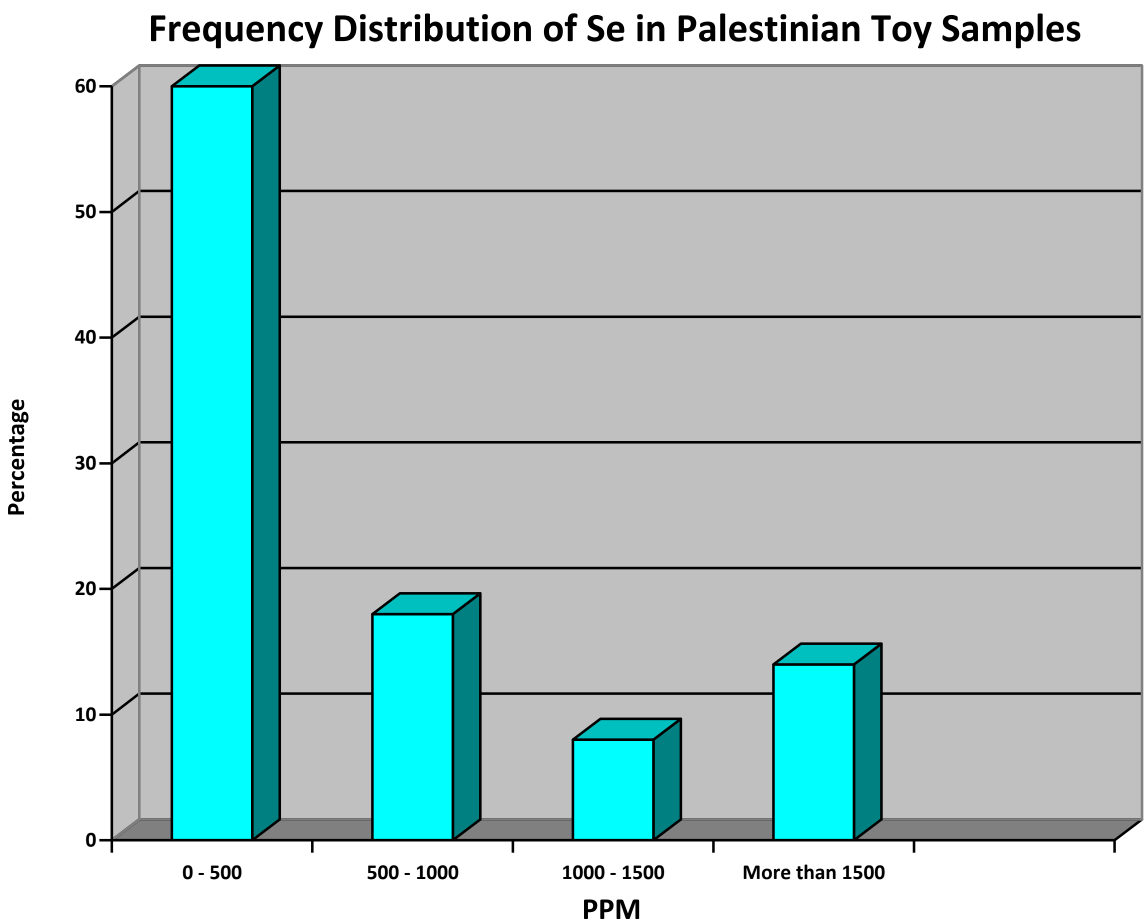

Figure 4.8 Frequency of Se in Palestinian Toy samples

Arsenic

The results of arsenic metal concentration are shown in Table 4.11 Forty two percent of the samples (21 samples out of 50) contain arsenic concentration more than 25 ppm or mg/kg. This means that 42% of the samples contain high Arsenic concentration above the maximum allowable value. Arsenic concentrations were ranged from (1.04to 2486) ppm (mg/kg) with an average of113.83ppm.

Table 4.11 Toy samples with arsenic concentration >25ppm (mg/kg)

Description	Arsenic	PVC	Color
T1(Lion)	471.37	Yes	Yellow
T2 (Water gun)	1858.16	Yes	Yellow + Orange
T3 (Barbie doll)	511.60	Yes	Gold + Brown
T4(Toy train)	44.49	Yes	Red + Black
T5(Necklace)	542.90	Yes	Green + Blue
T6 (Bracelet)	220.00	Yes	Gold + Silver
T7Beads gun)	2486.50	Yes	Black + Green
T9(Dinosaur)	39.80	Yes	Grey + Black
T11(Elephant)	105.20	Yes	Green + Grey
T15(Ambulance)	42.88	Yes	Red + White
T17(Giraffe)	57.17	Yes	White + Brown
T21(Truck car)	203.45	Yes	Green + Blue)
T23 (Ox)	66.71	Yes	Orange
T25(Apple)	117.15	Yes	Red + White
T26(Mobile)	39.15	Yes	White + Blue
T28(Pink mirror)	111.56	Yes	Pink
T29(Basketball)	43.08	Yes	Deep Orange
T34(Plastic ring)	191.60	Yes	Red
T35(Ball cilia)	89.30	Yes	Purple
T37(Telephone)	49.90	Yes	Black
T38(Caterpillar)	48.00	Yes	Deep Yellow

It was quite clear that the amount of arsenic in children toy samples included in Table 4.12, is very high compared to what is universally allowed, and there is no sufficient and convincing justification for the presence of such large amounts in toys.

It is fully recognized that the arsenic and its compounds in spite of their high toxicity have many uses such as wood preservation, fertilizers, fireworks, herbicides, and insecticides, electronics industry,and semiconductors that are used for solar cells,…etc.

There are some pigments that may contain arsenic or some of its compounds, such as Paris Green (copper acetoarsenite), that used as a pigment, despite its toxicity. It is also used as a blue colorant for fireworks (ASTDR, 2005), (IARC, 1989, 2004). The color of Paris Green is said to range from a pale, but vivid, blue green when very finely ground, to a deeper true green when coarsely ground. Also anti- micro-organisms and bacteria (Biocides) that may adhere to some PVC plastic products which touch the water, often containing arsenic compounds, but toys of this kind are few and limited use.

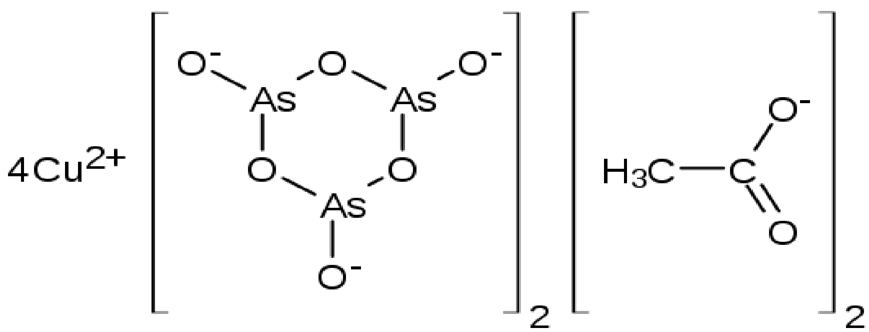

Figure 4.9 the chemical formula of Paris green (copper acetoarsenite)

Source (www.gamblincolors.com/.../pdf/GamblinStudioNote)

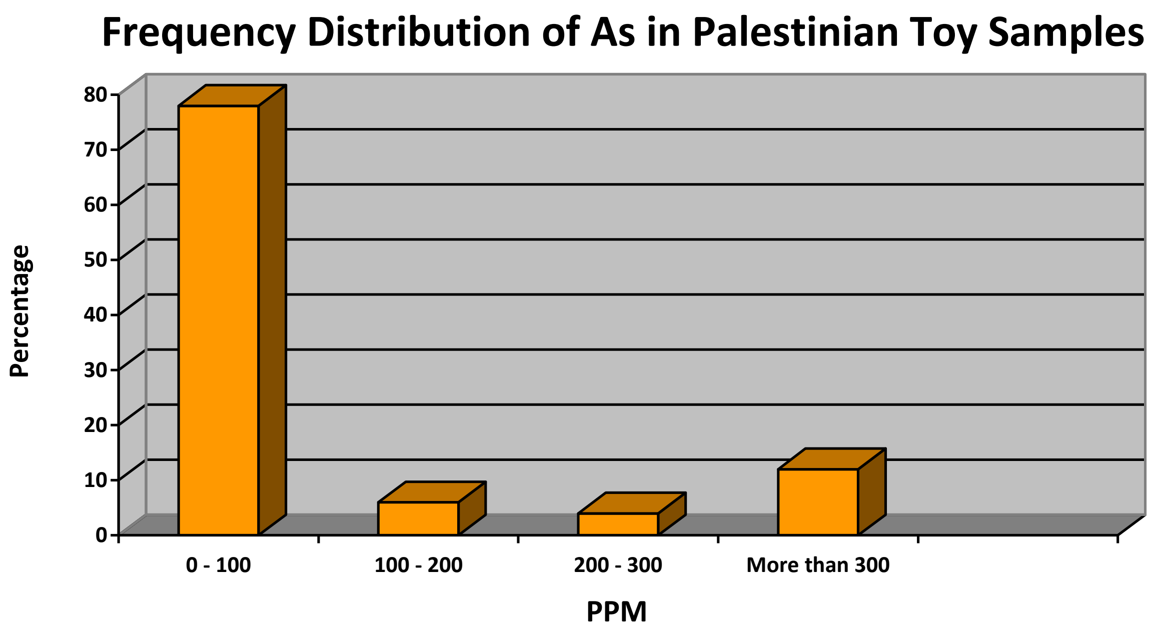

Figure 4.10 Frequency of As in Palestinian Toy samples

4.3 Heavy metal concentrations in the toy samples from Israeli market

As shown in table 4.12 below, the content of all toys samples from heavy metals is less than the maximum allowable international values except for one. Sample number S6, which is a deep yellow JCP Tractor toy, was found slightly higher than the maximum allowable values. The Lead and cadmium total content in this sample is **96.7 and 75.9** ppm, and both values slightly exceeded the maximum allowable international limit , which it is **90** and **75** ppm respectively.

Concentrations of heavy metals in the toys ranged from **2.8 to 96.7 ppm** for Pb with an average value equal to **39.2**ppm and from **4.5 to 75.9**with an average value equal to **36.9** for Cadmium, and from **7.15 to 59** with an average value equal to **36.87** for chromium, and from **3.2 to 25** with an average value equal to **3.62** for mercury**,** and from **0.0 to 22.4** with an average value equal **4.95** for arsenic, and from**0.71 to 342** with an average value equal to **93.9** for Selenium, and from **14.0 to 489.0** with an average value equal to **156.29** for Barium, and finally from **16.0 to 500**) with an average value equal to **159.56** for Zinc.

Table 4.12 concentrations of eight heavy metals in Seventeenth Israeli toy samples

Sample Code	**Description**	**Color**	**Pb**	**Cd**	**Cr**	**Hg**	**As**	**SE**	**Ba**	**Zn**
S1	Duck	Yellow +Blue	73.0	51.5	49.3	25.0	16.0	342.0	411.5	96.0
S2	Lorry Car	Green+ yellow	18.0	69	57	11.8	21.9	219.0	253	473.0
S3	Ox	Orange	86.2	66.7	59	6.3	13.0	99.7	456	316.0
S4	Caterpillar	Deep Yellow	90.0	71.2	44.3	15.3	22.4	217.3	489	488.0
S5	Toy Gun	Black	14.0	33.00	58.0	3.2	11.2	99.8	218.2	500.0
S6	JCP tractor	Deep yellow	96.7	75.9	61.0	ND	ND	38.5	95.0	111.4
S7	Mobile	Red+ Yellow	41.2	27.60	43.8	ND	ND	17.5	113.1	<DL
S8	House	Blue +Yellow	37.8	41.20	39.0	ND	ND	54.3	83.9	92
S9	Cup	Red	13.2	5.60	<DL	ND	ND	0.7	15.6	25.3
S10	Silicon Balls	Many colors	23.1	14.70	11.5	ND	ND	18.3	24.16	16.0
S11	Lego	Many colors	2.8	4.50	11.9	ND	ND	1.0	35.4	71.0
S12	Telephone	Red +White	28.4	18.60	24.1	ND	ND	84.0	117	58.0
S13	motorcycle	Grey +Blue	48.2	73.20	57.6	ND	ND	214.0	154	66.9
S14	Doll Toy	Brown	11.0	9.30	14.8	ND	ND	29.0	41.2	110.0
S15	Dog	Brown	6.9	8.36	7.15	ND	ND	42.0	63	102.0
S16	Plane	Green +White	9.5	12.80	10.1	ND	ND	75.3	14.0	114.0
S17	Tractor	Green + Yellow	39.7	42.00	58.3	ND	ND	44.0	72.3	88.9

As shown in Figure 4.11 and Figure 4.12 below, it is quite clear, that the concentrations of heavy metals total content in Palestinian toys samples are much higher than their Israeli counterparts. and the percentage of Israeli toy samples exceeded international allowable values is less than 5% , while it is more than 40% in some Palestinian toys samples for some heavy metals.

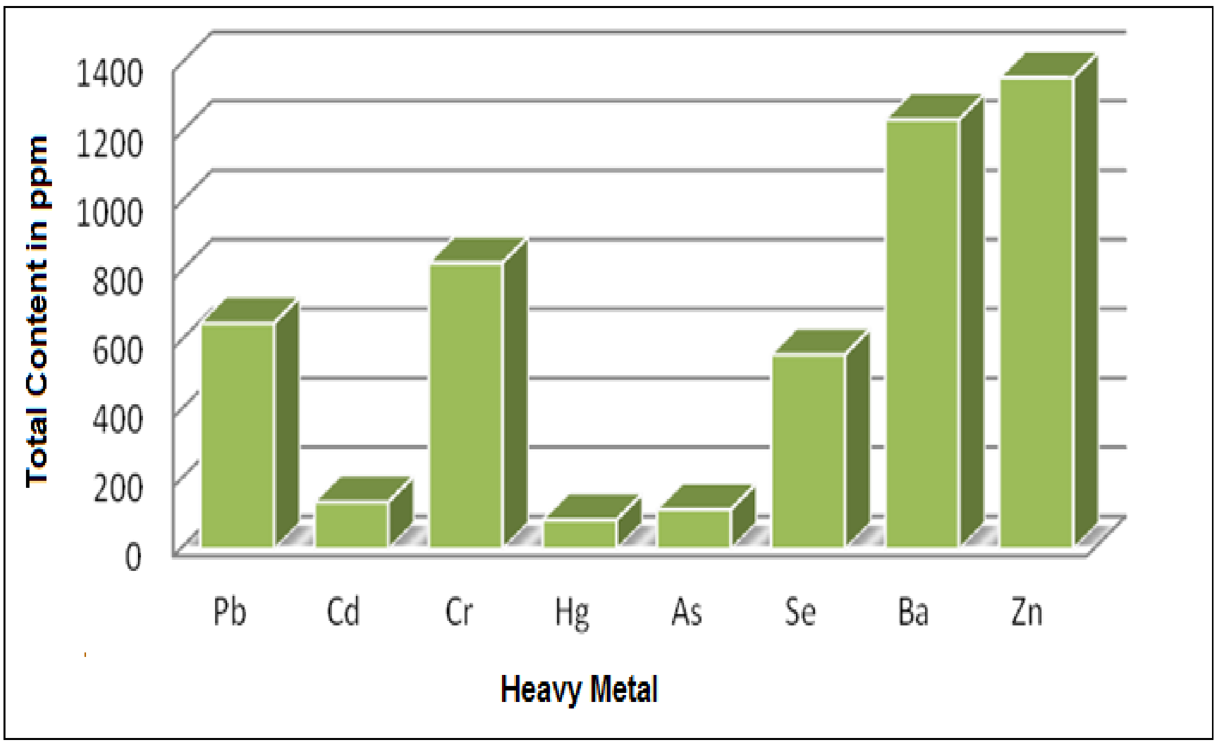

Figure 4.11The average of heavy metals total content in Palestenian toy samples

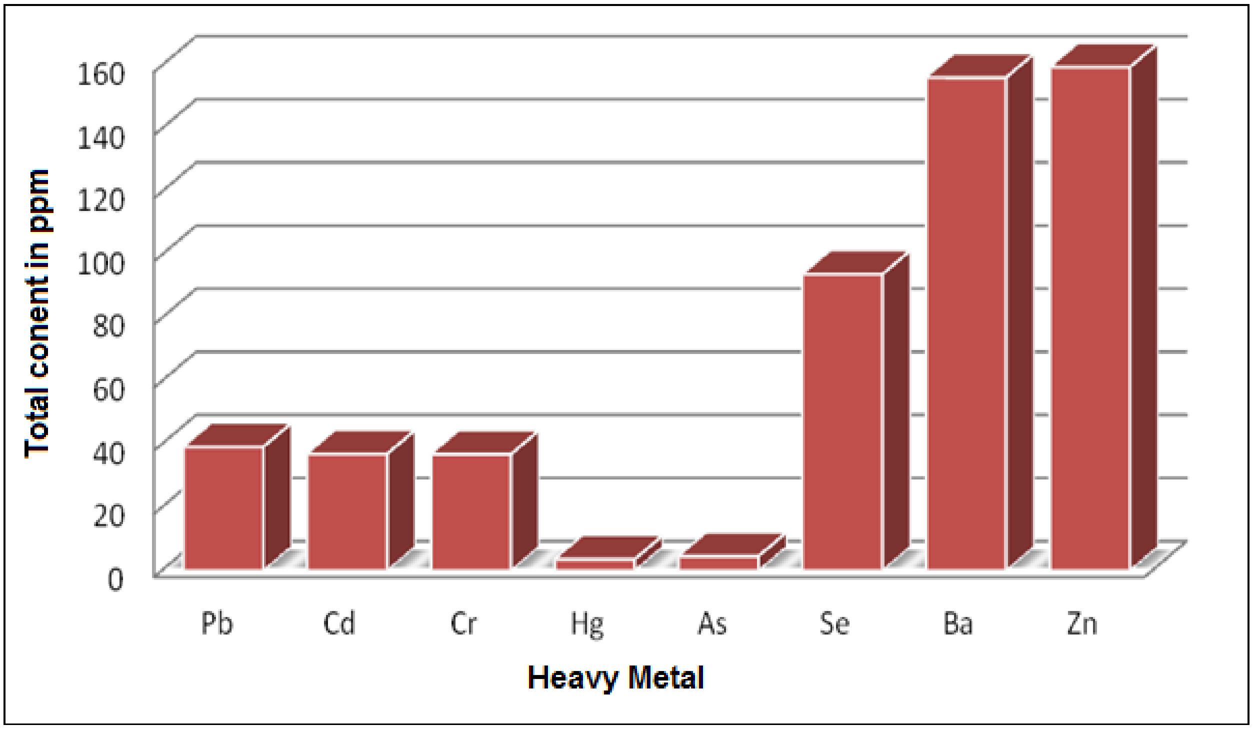

Figure 4.12 The average of heavy metals total content in Israeli toys samples

4.4 Migration rates Experiment

Migration rate is the amount of heavy metal which is released from the toy or article when it is submerged in artificial Saliva solution. The artificial Saliva solution used in the experiment as mentioned above was consist of the following materials (Methyle-p-hydroxybenzoate2.00g/1, Nacarboxymethyle cellulose 10g/1$MgCl_2.6H_2O$ 0.059g/1,KCl 0.625g/1, $CaCl_2.2H_2O$ 0.166g/1,K_2HPO_4 0.804g/1, KH_2PO_4 0.32g/1, PH 6.75 . Duration of the dipping samples was 8hr. This is intended to simulate chewing and swallowing the parts of toys or plastic items.

The migration rate results of eight heavy metals from dipped samples was as shown in table Table 4.13 below :

Table 4.13 The migration rate of eight heavy metals from 10 toy sample in artificial saliva

Sample code	Pb	Cd	Cr	Hg	As	Se	Ba	Zn
T6	9.70	11.20	14.9	0.00	3.4	23.80	51.0	41.2
T9	18.50	24.00	19.2	0.60	9.2	59.00	53.20	22.4
T13	32.10	30.20	24.1	ND	12.80	102	66.70	41.5
T14	11.20	14.20	10.5	ND	15.30	49.90	67.90	66.8
T21	9.40	11.30	8.9	ND	13.70	55.40	89.30	112.1
T25	27.30	25.10	20.5	ND	9.30	86.10	41.20	15.0
T26	35.80	31.40	28.8	ND	7.36	63.00	56.40	33.8
T30	45.20	40.20	33.7	ND	11.50	48.00	100.90	62.3
T37	19.50	21.50	19.2	6.10	14.50	19.70	78.30	92.1
T38	25.30	22.60	21.1	2.90	8.90	45.90	55.40	100.5
T40	17.60	19.30	16.4	0.52	21.20	55.82	38.10	45.1

None of the values in the table 4.13 above had exceeded the international maximum allowable limit, which is the boundary between safety and danger. We must take into account that the child does not use the toy only once, but many times with varying periods. The child also plays with more than one toy at the same time. There are always possibilities for cumulative effects. All of these toxins may accumulate in the body of the child and with time may exceed the maximum allowed. At this point the child is in real danger.

Chapter Five

Conclusion & Recommendations

5.1 Conclusion

This study showed beyond any reasonable doubt, that the plastic toys sold in Palestinian markets do contain concentrations of heavy metals higher than the internationally maximum allowable table 5.1 clearly shows this matter.

Table 5.1 Toy samples sold in Palestinian market that contains heavy metals concentration higher than the maximum allowable limits (MAL).

Sample code	**Pb**	**Cd**	**Cr**	**Hg**	**AS**	**Se**	**Ba**	**Zn**
MAL(ppm)	**90**	**75**	**60**	**60**	**25**	**500**	**1000**	**1000**
T1	1775.70		471.37		471.37	1778.00		3377.00
T2		113.40	1858.16		1858.16	1080.70		7526.80
T3		139.40	511.60		511.60	1292.00		3443.90
T4					44.09			1337.00
T5			524.20		542.09			1075.27
T6		251.69	220.40		220.40	868.20		10725.00
T7			2468.50		2486.50			
T8								
T9	1431.00				39.80			1560.00
T10							16074.40	3875.80
T11	611.96		105.20		105.20			1933.90
T12							5768.00	
T13		324.50						3875.80
T14	5467.00							
T15	1886.64				42.88		5530.70	
T16	5467.78	436.42	295.60				3403.60	2119.80
T17					57.17			
T18								
T19	6036.00	193.78						2110.40
T20		289.60				773.77		1000.00
T21	661.76		203.45		203.45	508.00		2017.00
T22	109.85					1700.40		
T23	2919.69		66.10		66.70	884.40		
T24	1405.00							

Continued the table 5.1

T25			117.15		117.5			1110.40
T26					39.15			
T27								
T28					111.56			
T29	2044.70	100.50			43.80	980.00	2550.00	
T30	177.15							
T31	397.30					1000.81		
T32			359.87			530.00		
T33	1021.60							
T34	975.50		191.6		191.60			
T35			89.30		89.30		2066.50	
T36			89.15				9159.00	
T37	1021.60				49.90		5606.00	
T38	8195.60		194.00		48.00	553.00		
T39	1761.00							
T40		256.35					1670.04	
T41		420.00				693.00		4618.00
T42	8195.00	150.18						1000.00
T43	1761.00			63.6		2833.00		
T44								
T45		298.66		64.60			1325.90	3789.00
T46		349.44						
T47		90.43						
T48								1369.00
T49						599.30		
T50						618.40		1157.00

The presence of heavy metals in the toys that have been purchased from the Palestinian market were in the range of **(0.76 - 8195.6), (0.47-436.42), (6.76 – 2468.0), (0.118 - 85.9), (1.04 - 2486), (16.6 - 2833), (6.76 – 9255.0) and (9.5 – 7625.80)** mg/Kg for Pb, Cd, Cr, Hg, As, Se, Ba, and Zn respectively. Both PVC and non-PVC toys contain heavy metals but the concentration of these metals in non-PVC toys were found generally less than that of PVC toys.

The present study reveals that **42%** of the toy samples show high concentration (above international limits) of Lead, **30%** of Cadmium, **34%** of Chromium,**6%** of mercury, **42%** of arsenic, **32%** of selenium, **22%** of barium and **40%**of zinc respectively .

This study reveals that about **94%** of toy samples from Israeli market are safe (one sample out of seventeenth contains lead and cadmium slightly higher than MAL. None of the migration rate of eight heavy metals from toy samples submerged in artificial saliva, had exceeded the international maximum allowable limit, which is the boundary between safety and danger.

The problem of toys poisoning has widely been recognized. This problem needs a special attention from the responsible persons especially in Palestine.

5.2 Recommendations

Based on our study, the Palestinian government at all levels should take the following actions:

1) - Act quickly to adopt policies to protect consumers and ban the use of PVC in toys and children's products.

2) - Eliminate the purchase of products and packaging that contain lead, cadmium, and other hazardous heavy metals and chemical additives in toys and children's products.

3) - Label the material content of toys so that consumers can easily identify safer products. Toys made with PVC should be labeled "made with PVC." Toys made without PVC should be labeled "PVC-free." By requiring all PVC products to be labeled, consumers can readily identify which products contain PVC and its additives and which are safe to purchase.

4) - Conduct a public campaign to educate consumers about the risks posed by plastic made toys.

5) - Conduct an independent study on the concentrations of phthalate in plastic toys, because it's riskiness not less than that of heavy metals.

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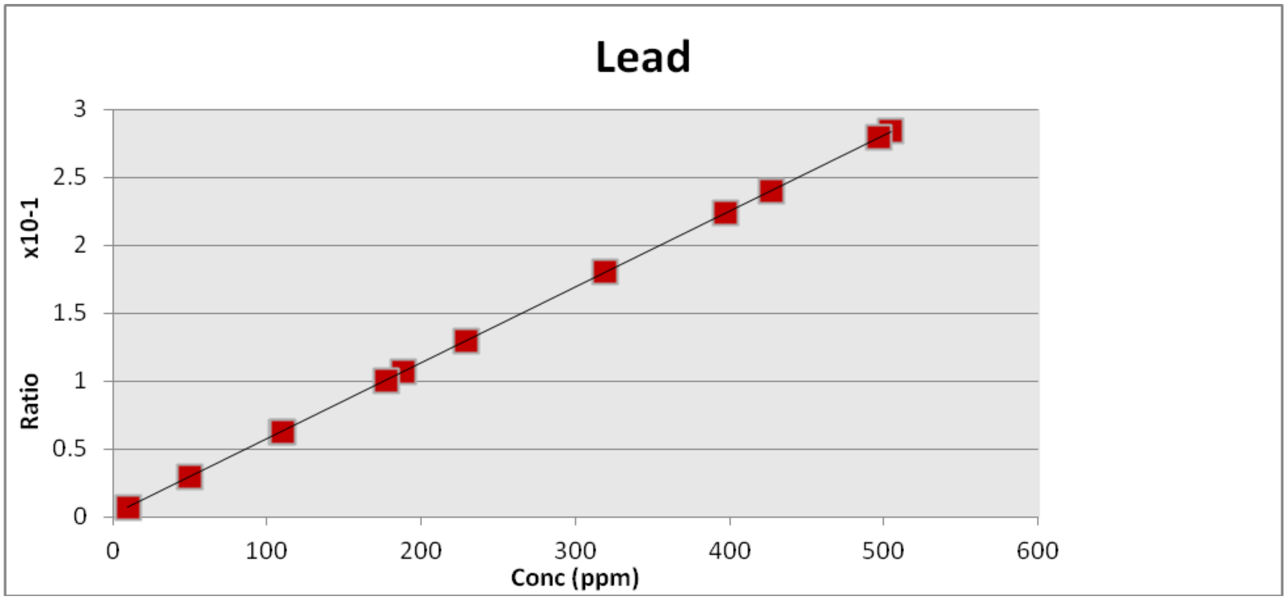
Appendix A

Calibration curve for various lead concentrations using ICPMS

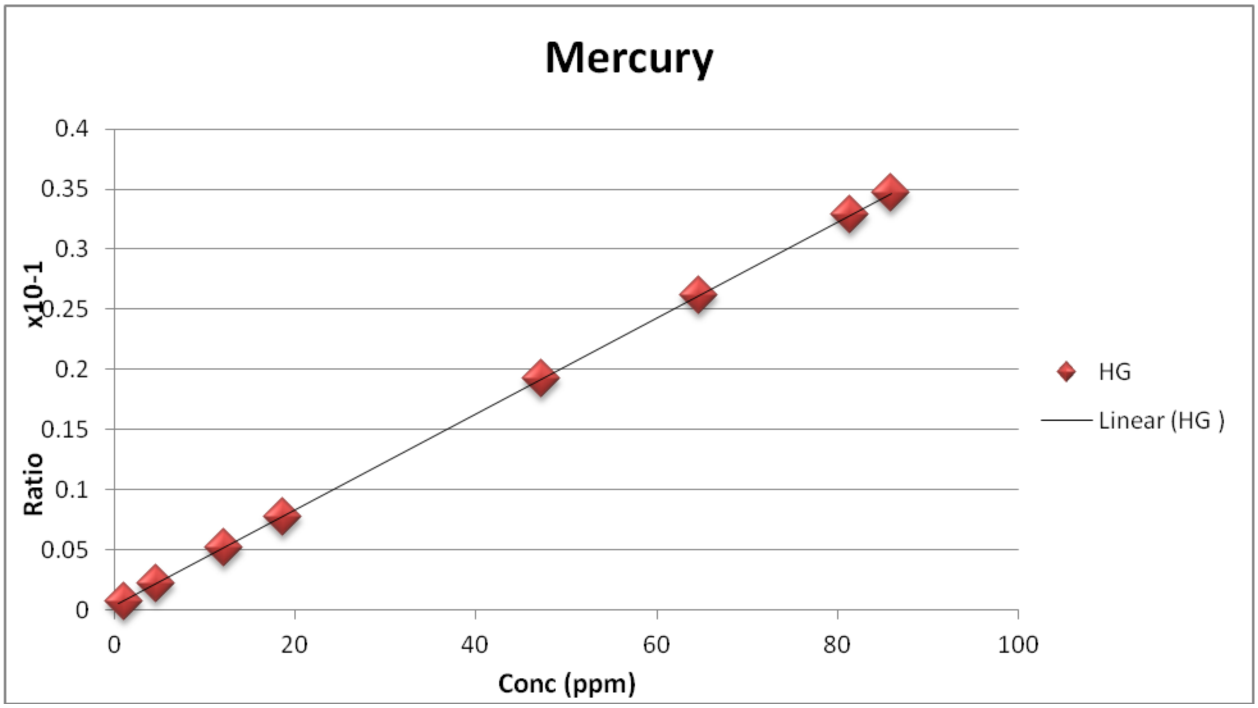


$$Y = (0.0056 * X) + 0.0133$$

Ratio= Instrument Response (account/time)

R=0.9990

Calibration curve for various mercury concentrations using ICPMS

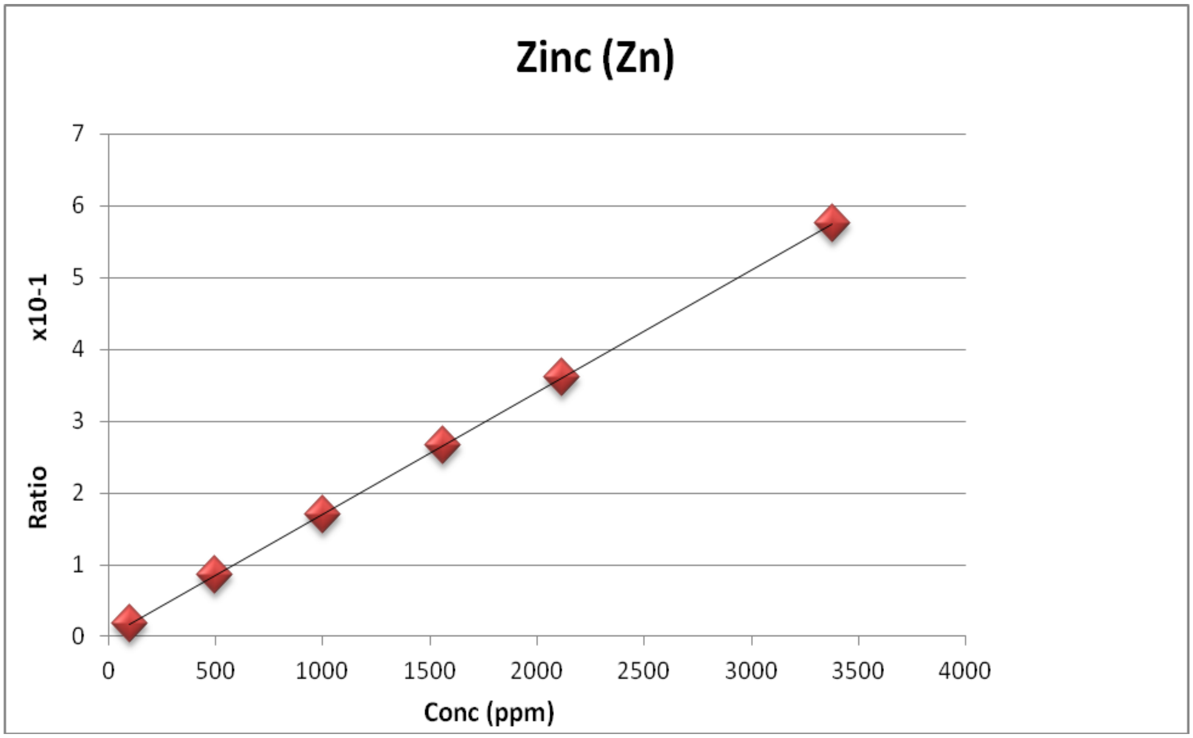


Y=0.0040 *X + 0.0031

Ratio= Instrument Response (account/time)

R = 0.9992

Calibration curve for various zinc concentrations using ICPMS

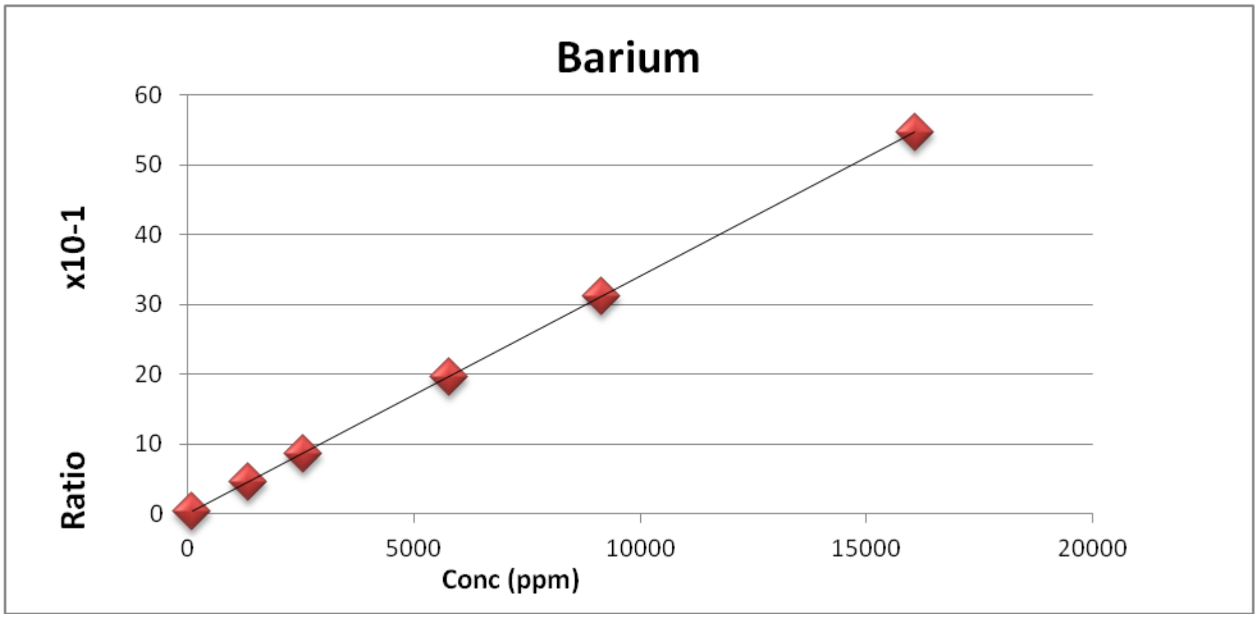


Y= (0.00338*X) + 0.0049

Ratio= Instrument Response (account/time)

R= 0.9410

Calibration curve for various barium concentrations using ICPMS

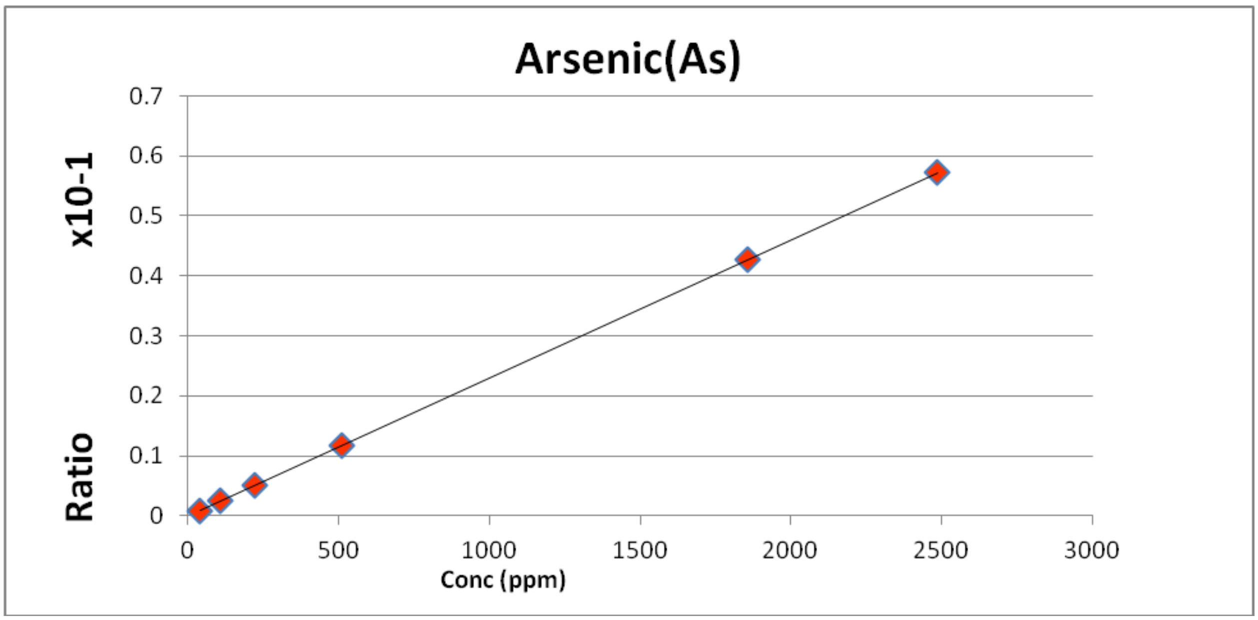


Y = 0.0034 * X + 0.0044

Ratio= Instrument Response (account/time)

R = 0.9090 ,

Calibration curve for various arsenic concentrations using ICPMS

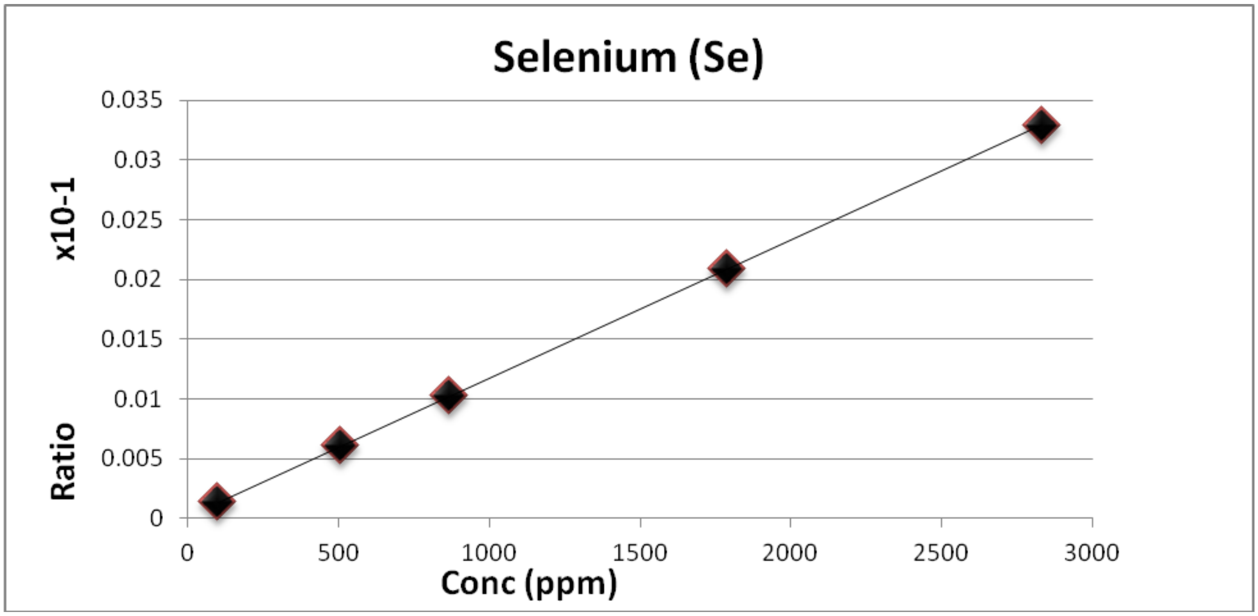


Y = 2.3019 E-004 * X +3.9034 E-005

Ratio= Instrument Response (account/time)

R = 0.9990

Calibration curve for various selenium concentrations using ICPMS

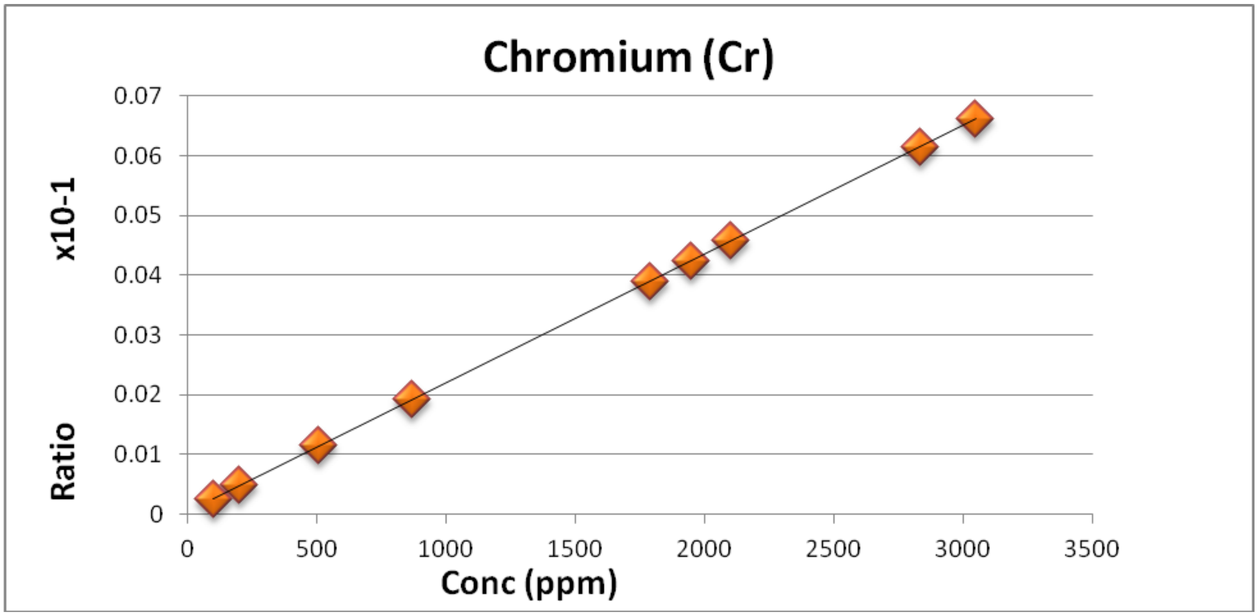


Y = 1.1552E-005 *X +2.0628E-004

Y= Instrument Response (account/time)

R = 0.9987

Calibration curve for various chromium concentrations using ICPMS

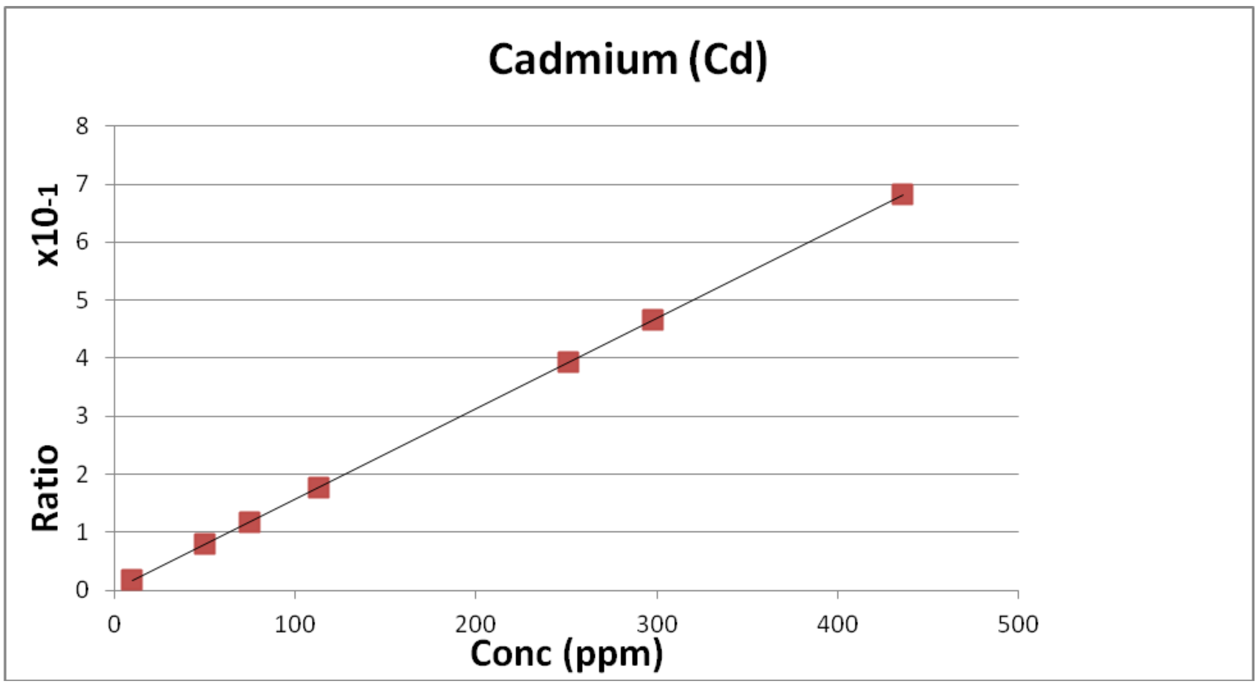


Y = 2.1552E-005 *X +4.0628E-004

Ratio= Instrument Response (account/time)

R = 0.9987

Calibration curve for various cadmium concentrations using ICPMS



Y= (0.0156 * X) + 0.0144

Ratio= Instrument Response (account/time**)**

R=0.9880

Appendix B

The Toys samples photos from Palestinian market


T1


T2


T3


T4


T5


T6


T7


T8


T9


T10


T11


T12


T13


T14

T15

T16

T17

T18

T19

T20

T21

T22

T23

T24

T25

T26

T27

T27

T28

T29




T30 T31 T32 T33

T34 T35 T36 T37



T38 **T39** **T40** **T41**




T42

T45 T46 T47 T48

T49 T50

The Toys samples photos from Israeli market

S1 **S2** **S4**

S5 **S6** **S7**

S8 **S9** **S10**

S11 **S12** **S13**

S14 **S15** **S16**

S17 **S3**

الخلاصة

تعرض الأطفال للمعادن الثقيلة ما زال يشكل مشكلة صحية بالغة القلق ، هذه الدراسة قامت بقياس تراكيز ثمانية من المعادن الثقيلة في لعب الأطفال البلاستيكية المتواجدة في الأسواق الفلسطينية المحلية ،حيث تم تحليل ما يزيد عن خمسين عينة من اللعب المصنوعة من البلاستيك لقياس تراكيز كل من: الرصاص ، الكادميوم ، الكروم ، الزئبق ، الزرنيخ ، السيلينيوم ، الباريوم والزنك في هذه العينات .
اختيرت الألعاب عشوائياً من المنتجات المتواجدة في محلات الجملة والأكشاك والباعة المتجولين في أسواق ثلاثة من كبريات المدن الفلسطينية وهي نابلس والخليل ورام الله ، تم إخضاع العينات لفحص (بلستين) للتأكد من أنها مصنوعة من مبلمر البولي فنيل كلورايد أم من غيره غيره من المبلمرات ، بعدها تم إضافة حمض النيتريك المركز وفوق أكسيد الهيدروجين ، ليتم إذابتها بتأثير الضغط والحرارة في جهاز المايكرويف المغلق (Closed acid digestion) وذلك كخطوة ضرورية لإعداد العينات لجهازICPMS .

ومن ثم تم قياس تركيز العناصر المذكورة أعلاه بواسطة جهازICPMS، وقد كانت معدلات هذه العناصر كالتالي: **(٠,٧٦-٨١٩٥,٦)**، **(٠,٤٧-٢٥٦)**، **(٦,٧٦-٧٧٨٦,٣)**، **(٠,١١٨-٨٥,٩)**،**(١,٠٤-٢٤٨٦)** **(١٦,٠٦-٤٤١٥)** ، **(٦,٧٦-١٦٠٧٤)** ، **(٩,٥-١٦٦٤٢)** ملغم/كغم لكل من الرصاص ، الكادميوم، الكروم، الزئبق، السيلينيوم، الباريوم والخارصين على التوالي.

وقد تبين أن كلاً من الألعاب المصنوعة من البولي فينيل كلورايد وتلك المصنوعة من غير البولي فينيل كلورايد تحتوي على نسب من هذه العناصر ، غير أن الألعاب المصنوعة من البولي فينيل كلورايد كانت تراكيز المعادن الثقيلة فيها أعلى .

أظهرت هذه الدراسة أيضاً أن **42%** من عينات الالعاب تحتوي على كمية من الرصاص أكبر من القيمة القصوى المسموح بها دولياً، و**30%** من الكادميوم،و**٣٤%** من الكروميوم، **٦%** من الزئبق، **٤٢%**من الزرنيخ، و**٣٢%** من السيلينيوم، **20%** من الباريوم و**40%** من الزنك

بالمقابل ، تم قياس تراكيز العناصر الثقيلة الثمانية المذكورة اعلاه في ١٧ عينة من الألعاب الإسرائيلية ليتم مقارنتها بنظيراتها من الألعاب الفلسطينية ، وقد وجد أن ٩٥% من الألعاب الإسرائيلية كانت آمنة وتراكيز العناصر االثقيلة الموجودة فيها أقل من الحد المسموح به دولياً .

بشكل عام هذه التراكيز العالية من المعادن الثقيلة في الألعاب الفلسطينية تشكل خطراً صحياً بالغاً على الأطفال وتعرض حياتهم للخطر . بناءً عليه وفي ضوء ما بين أيدينا من البيانات، فإننا نوصي السلطات المختصة بالآتي:

١)- أن تتبنى سياسة تعمل على حماية المستهلكين وذلك من خلال منع استيراد اللعب البلاستيكية المصنوعة من مبلمر ال PVC

٢)- القيام بحملة شعبية تهدف الى توعية المواطنين بمخاطر هذه الألعاب .

٣)- التخلص من الألعاب والمنتجات البلاستيكية التي تحتوي تراكيز أعلى من المطلوب من المعادن الثقيلة المتواجدة في السوق الفلسطيني.

٤)- مراقبة الاطفال من قبل ذويهم عند استخدامهم للعب البلاستيكية والتقليل قدر الامكان من مضغها أو امتصاصها.

٥)- إعداد دراسة مستقلة تقوم بقياس تراكيز الفثيلات في لعب الاطفال لأنها لا تقل خطورة عن المعادن الثقيلة على كل من البيئة وصحة الانسان.