Sudan University of Science and Technology
Collage of Graduate Studies

Studying Heavy Metal Assessment of Some Soft Plastic Toys Imported into Sudan from China and Taiwan

دراسة تقييم العناصر الثقيلة في بعض الألعاب البلاستيكية الموردة للسودان من الصين وتايوان

A thesis submitted for partial fulfillments of the requirement of the degree of science master in physics

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الآيــــــــة

بسم الله الرحمن الرحيم

قَالَ تَعَالَى: ﴿ قَالُوا۟ سُبْحَـٰنَكَ لَا عِلْمَ لَنَآ إِلَّا مَا عَلَّمْتَنَآ ۖ إِنَّكَ أَنتَ ٱلْعَلِيمُ ٱلْحَكِيمُ ﴿٣٢﴾ ﴾

صدق الله العظيم

{ سورة البقرة ﴿٣٢﴾ }

Dedication

I dedicate to all those who contributed in education

Dedicate to my father and soul my mother, to my husband, and my twins.

To my brothers, sister, my teacher and my colleagues.

To all of you i dedicate this modest effort Researcher

Acknowledgements

Thank God first and foremost

Thank everyone who helped me in my career complete educational and completion of this research, especial thanks to my husband for his endless support to accomplish this research.

I thank the professors in Sudan University of Science and Technology Faculty of Science, Department of Physics

And thanks my supervisor, Dr. Rawia Abdelgani

God bless all of us

Abstract

China and Taiwan made toys were analyzed to determine the levels of heavy metals (Pb, Cd, Hg, Ni, Cu, Zn, Cr, Co and Mn) in the products. Twenty one Toy samples were randomly selected from products available in the shops at Khartoum. The toy samples were tested for PVC before analysis. Concentrations of the selected heavy metals were determined ppm and 3sigma. Samples tested positive for PVC. Concentrations of heavy metals in the toys ranged from for Pb, Cd, Ni, Cu, Zn, Cr, Co and Mn respectively. Both PVC and non-PVC toys contain.

Heavy metals but the concentration of these metals in non-PVC toys is generally less than that of PVC toys. The present study reveals that most samples in agreement with standard concentration except two elements vacillates of the toy samples show high concentration (above USFDA limit) of Hg, Cr and other metals determined; this poses a threat to children exposed to such toys.

المستخلص

في هذه الدراسة تم تحليل عينات من الألعاب الموردة من الصين وتايوان لتحديد العناصر الثقيلة في هذه المواد Pb, Cd, Hg, Ni, Cu, Zn, Cr, Co and Mn .

تم إختيار (21) عينة عشوائيا متاحة من الأسواق المحلية بمدينة الخرطوم، وقد تم إختبار PVC قبل التحليل. حددت العناصر الثقيلة بتراكيز ppm و 3sigma ووجدت العناصر التالية في العينات المختلفة Pb, Cd, Hg, Ni, Cu, Zn, Cr, Co and Mn .

الدراسة الحالية توضح أن معظم العناصر تتفق مع التراكيز القياسية المسموح بها من قبل الهيئة القومية السودانية للمواصفات والمقاييس عدا عنصري الزئبق والكروم، ويمكن أن يمثلا خطرا بالنسبة للاطفال عند تعرضهم لهذه العناصر.

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Chapter One

Introduction

1.1 Toys

A toy is an item that is used in play, especially one designed for such use. Playing with toys can be an enjoyable means of training young children for life in society. Different materials like wood, clay, paper, and plastic are used to make toys. Many items are designed to serve as toys, but goods produced for other purposes can also be used. For instance, a small child may fold an ordinary piece of paper into an airplane shape and "fly it". Newer forms of toys include interactive digital entertainment. Some toys are produced primarily as collectors' items and are intended for display only. The origin of toys is prehistoric; dolls representing infants, animals, and soldiers, as well as representations of tools used by adults are readily found at archaeological sites. The origin of the word "toy" is unknown, but it is believed that it was first used in the 14th century. Toys are mainly made for children [1]. The oldest known doll toy is thought to be 4,000 years old [2].

Playing with toys is considered to be important when it comes to growing up and learning about the world around us. Younger children use toys to discover their identity, help their bodies grow strong, learn cause and effect, explore relationships, and practice skills they will need as adults. Adults on occasion use toys to form and strengthen social bonds, teach, help in therapy, and to remember and reinforce lessons from their youth.

1.2Research Problem

Certain plastics are known to contain toxic chemicals which have negative impacts on human health. Children are particularly vulnerable to toxic chemicals since their systems and organs are still developing. Young children are also at greater risk since they often insert plastic objects into their mouths. Baby bottles, Sippy cups, teething rings, and toys are often made with phthalates and Bisphenol A (BPA). These two toxic ingredients in plastics are of particular concern, as research increasingly shows that these chemicals mimic or suppress hormones (e.g., estrogen and testosterone) and disrupt normal development and growth of children.

1.3Aims

To evaluate the concentration and percentages of elements in those toys

1.4 Previous Studies

- Gillian Zaharias Miller (2015) concluded that:

Over 100 plastic toys from the 1970s and 1980s, both polyvinyl chloride ("vinyl") and non-vinyl, were analyzed in the study described here using a handheld X-ray fluorescence spectrometer to quantify hazardous metal content. A sampling of recent vinyl toys was also tested. The majority of non-vinyl samples were Fisher Price brand toys. The vinyl toys consisted largely of Barbie dolls and other dolls. Overall, lead or cadmium was found in 67% of vintage plastic toys, frequently at concentrations exceeding current U.S. and European limits. Arsenic was detected at levels of concern in 16% of the samples. In the non-vinyl toys, heavy metal content was found to correlate with certain colors of plastic.

The likely sources of the detected metals are discussed. None of the contemporary vinyl toys contained detectable cadmium, lead, or arsenic. Given that vintage toys remain in widespread use by children in homes and other locations, the results illuminate a potential source of heavy metal exposure for children [3].

1.5 Research layout

This research has come into four chapters, chapter one is an introduction, chapter two theoretical background, chapter three X-Ray Fluorescence, while Chapter four the practical

Chapter Tow

Theoretical Background

2.1 Introduction

Most children have been said to play with whatever they can find, such as sticks and rocks. Toys and games have been unearthed from the sites of ancient civilizations. They have been written about in some of the oldest literature. Toys excavated from the Indus valley civilization (3010-1500 BCE) include small carts, whistles shaped like birds, and toy monkeys which could slide down a string [4].

The earliest toys are made from materials found in nature, such as rocks, sticks, and clay. Thousands of years ago, Egyptian children played with dolls that had wigs and movable limbs which were made from stone, pottery, and wood [5].In Ancient Greece and Ancient Rome, children played with dolls made of wax or terracotta, sticks, bows and arrows, and yo-yos. When Greek children, especially girls, came of age it was customary for them to sacrifice the toys of their childhood to the gods. On the eve of their wedding, young girls around fourteen would offer their dolls in a temple as a rite of passage into adulthood [6,7].

The oldest known mechanical puzzle also comes from Greece and appeared in the 3rd century BC. The game consisted of a square divided into 14 parts, and the aim was to create different shapes from these pieces. In Iran "puzzle-locks" were made as early as the 17th century (AD).

2.2 Types of Toys

2.2.1 Construction sets

The Greek philosopher Plato wrote that the future architect should play at building houses as a child. A construction set is a collection of separate pieces that can be joined together to create models. Popular models to make include cars, spaceships, and houses, The things that are built are sometimes used as toys once completed, but generally speaking, the object is to build things of one's own design, and old models often are broken up and the pieces reused in new models. The oldest and, perhaps most common construction toy is a set of simple wooden blocks, which are often painted in bright colors and given to babies and toddlers. Construction sets such as Lego bricks and Lincoln Logs are designed for slightly older children and have been quite popular in the last century. Construction sets appeal to children (and adults) who like to work with their hands, puzzle solvers, and imaginative sorts [8].

Some other examples include Bayko, Konstruk-Tubes, K'Nex, Erector Sets, Tinkertoys, and Meccano, and generic construction toys such as Neodymium magnet toys.

2.2.2 Dolls and miniatures

A doll is a model of a human (often a baby), a humanoid (like Bert and Ernie), or an animal. Modern dolls are often made of cloth or plastic. Other materials that are, or have been, used in the manufacture of dolls include cornhusks, bone, stone, wood, porcelain (sometimes called china), bisque, celluloid, wax, and even apples. Often people will make dolls out of whatever materials are available to them.

Sometimes intended as decorations, keepsakes, or collectibles for older children and adults, most dolls are intended as toys for children, usually girls, to play with. Dolls have been found in Egyptian tombs which date to as early as 2000 BC [8].Dolls are usually miniatures, but baby dolls may be of true size and weight. A doll or stuffed animal of soft material is sometimes called a plush toy or plushier. A popular toy of this type is the Teddy Bear. A distinction is often made between dolls and action figures, which are generally of plastic or semi-metallic construction and pose able to some extent, and often are merchandising from television shows or films which feature the characters. Modern action figures, such as Action Man, are often marketed towards boys, whereas dolls are often marketed towards girls. Toy soldiers, perhaps a precursor to modern action figures, have been a popular toy for centuries. They allow children to act out battles, often with toy military equipment and a castle or fort. Miniature animal figures are also widespread, with children perhaps acting out farm activities with animals and equipment centered on a toy farm [8].

2.2.3 Vehicles

Children have played with miniature versions of vehicles since ancient times; with toy two-wheeled carts being depicted on ancient Greek vases. Windup toys have also played a part in the advancement of toy vehicles. Modern equivalents include toy cars such as those produced by Matchbox or Hot Wheels, miniature aircraft, toy boats, military vehicles, and trains. Examples of the latter range from wooden sets for younger children such as BRIO to more complicated realistic train models like those produced by Lionel, Doepke and Hornby.

Larger die-cast vehicles, 1:18 scale, have become popular toys; these vehicles are produced with a great attention to detail [8].

2.2.4 Puzzles

A puzzle is a problem or enigma that challenges ingenuity. Solutions to puzzle may require recognizing patterns and creating a particular order. People with a high inductive reasoning aptitude may be better at solving these puzzles than others. Puzzles based on the process of inquiry and discovery to complete.may be solved faster by those with good deduction skills. A popular puzzle toy is the Rubik's Cube, invented by Hungarian Ernő Rubik in 1974. Popularized in the 1980s, solving the cube requires planning and problem-solving skills and involves algorithms. There are many different types of puzzles, for example a maze is a type of tour puzzle. Other categories include; construction puzzles, stick puzzles, tiling puzzles, transport puzzles, disentanglement puzzles, sliding puzzles, logic puzzles, picture puzzles, lock puzzles and mechanical puzzles [8].

2.2.5 Collectibles

Some toys, such as Beanie Babies, attract large numbers of enthusiasts, eventually becoming collectibles. Other toys, such as Boyd's Bears are marketed to adults as collectibles. Some people spend large sums of money in an effort to acquire larger and more complete collections. The record for asingle Pez dispenser at auction, for example, is US$1100[8].

2.2.6 Promotional merchandise

Many successful films, television programs, books and sport teams have official merchandise, which often includes related toys. Some notable examples are Star Wars (a science fiction film series) and Arsenal, an English football club. Promotional toys can fall into any of the other toy categories; for example they can be dolls or action figures based on the characters of movies or professional athletes, or they can be balls, yo-yos, and lunch boxes with logos on them. Sometimes they are given away for free as a form of advertising. Model aircraft are often toys that are used by airlines to promote their brand, just as toy cars and trucks and model trains are used by trucking, railroad and other companies as well. Many food manufacturers run promotions where a toy is included with the main product as a prize. Toys are also used as premiums, where consumers redeem proofs of purchase from a product and pay shipping and handling fees to get the toy. Some people go to great lengths to collect these sorts of promotional toys [9].

2.2.7 Digital toys

Digital toys are toys that incorporate some form of interactive digital technology [9].Examples of digital toys include virtual pets and handheld electronic games. Among the earliest digital toys are Mattel Auto Race and the Little Professor, both released in 1976. The concept of using technology in a way that bridges the digital with the physical world, providing unique interactive experiences for the user has also been referred to as "Phygital"[9].

2.2.8 Physical activity

A great many toys are part of active play. These include traditional toys such as hoops, tops, jump ropes and balls, as well as more modern toys like Frisbees, foot bags, astrojax, and Myachi. Playing with these sorts of toys allows children to exercise, building strong bones and muscles and aiding in physical fitness. Throwing and catching balls and Frisbees can improve hand-eye coordination. Jumping rope, (also known as skipping) and playing with foot bags can improve balance [9].

Chapter Three

X-Ray Fluorescence

3.1 Introduction

The potential use of x rays was appreciated soon after x rays were discovered. They early applications used Geiger-Mueller tubes and elaborate absorber arrays or crystal diffraction gratings. Later, advances in semiconductor detectors and associated electronics opened up the field of energy-dispersive x-ray fluorescence (XRF) analysis to find elements and concentration in samples. This chapter is concerned with

3.2 X-Ray Production

Continuous X-ray is produced by bombardment of electrons with metal samples. But characteristic X-rays originate from atomic transitions. In the stable atom electrons occupy discrete energy levels that are designated (in order of decreasing binding energy) K, L_1, L_2, L_3, M_1 …, M_5, N_1,…, N_7, and so forth. The binding energy is the energy that must be expended to remove an electron from a given orbit. The vacancy thus created is filled by an electron from an outer orbit. The resultant loss in energy may appear as an x ray whose energy is equal to the difference in the energies of the two electron states. For example, if a uranium K electron is removed from the atom and an electron from the L_3 level falls into its place, the energy of the emitted x ray is 98.428 keV (115.591 keV minus 17.163 keV). The x ray produced by this transition is designated. The K-series has a specific probability or intensity. The K-to-L_3 transition is the most probable, and other intensities are usually expressed relative to. Figure 3.1 depicts the transitions involved in the production of most abundant K and L rays [10].

Table (3-1) presents the major L lines of uranium and plutonium, along with their relative intensities. Figure (3.2) and 3.3 show the K and L x-ray spectra of uranium.

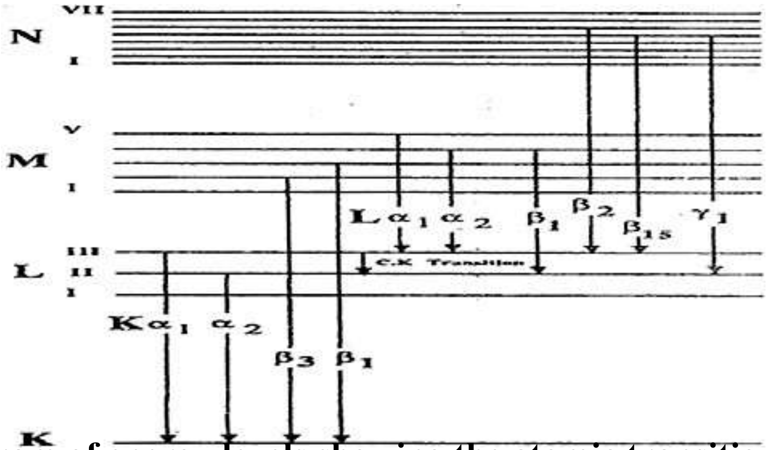

Figure (3.1) Diagram of energy levels showing the atomic transitions that produce the major K and L x rays (C.K. = CosterKronig)

Fluorescence yield is concerned with X-ray emission probability. All ionizations do not result in x-ray emission. The Auger effect is a competing mechanism of atomic relaxation. In this process, the atom regains energy stability by emitting an outer shell electron. The ratio of the number of emitted x rays to the total number of ionizations is called the fluorescence yield, where i designate the shell involved. Fluorescence yield increases with atomic number and is greater than 95% for K x rays of elements with Z > 78 .For a given element, the fluorescence yield decreases from the K series to the L and M series. The fluorescence yield can be approximated by:

$$W\omega_i = Z^4 / (A_i + Z^4) \qquad (3.1)$$

here A_i is approximately 10^6 for the K shell and 10^8 for the L shell, for a photon to eject an electron, the photon energy must be greater than or equal to the electron binding energy. For example, to ionize K electrons of plutonium, the energy of the excitation photon must be at least 121.82 keV [10].

Table (3.1) Energies and relative intensities of major K and L x ray for uranium and plutonium

Energies in KeV^a			
Transition Line (Final - Initial)		Uranium (%)^b	Plutonium (%)
	K - L_3	98.44 (100)	103.76 (100)
	K - L_2	94.66 (61.9)	99.55 (62.5)
	K - M_3	111.31 (22.0)	117.26 (22.2)
	K - M_2	110.43 (11.6)	116.27 (11.7)
	K - $N_{2,3}$	114.34, 114.57 (12.3)	120.44, 120.70 (12.5)
	L_3 - M_5	13.62 (100)	14.28 (100)
	L_3 - M_4	13.44 (10)	14.08 (10)
	L_3 - M_5	16.43 (20)	17.26 (20)
	L_3 - M_1	11.62 (1-3)	12.12 (1-3)
	L_2 - M_4	17.22 (50)	18.29 (50)
ఊ	L_2 - M_4	20.17 (1910)	21.42 (1-10)
	L_1 - M_3	17.45 (1-6)	18.54 (1-6)
	L_1 - M_2	16.58 (3-5)	17.56 (3-5)

[a] Calculated from table of Isotopes, Appendix III (L lines) (C. M. Lederer and V. S. Shirley, Eds., 7th ed. [John Wiley & Sons, Inc., New York, 1978])

[b] Intensities relative to either or in percent.

[c] Approximate only.

The fraction of photons, F, that interact with atomic electrons of a Particular material is given by:

$$F = 1 - \exp(-\mu \rho x) \tag{3.2}$$

Where:

μ = mass attenuate coefficient

ρ = density of sample

x = thickness of sample

If one plots the mass attenuation coefficient vs photon energy for a given element, sharp discontinuities (known as "absorption edges") are observed. Figure (3.6) shows the mass attenuation coefficient for uranium and plutonium. The edges indicate the sudden decrease in the photoelectric cross section for incident photon energies just below the binding energy of that particular electron state. The photo-electric interaction is the dominant process involved in photon-excited x-ray excitation [10].

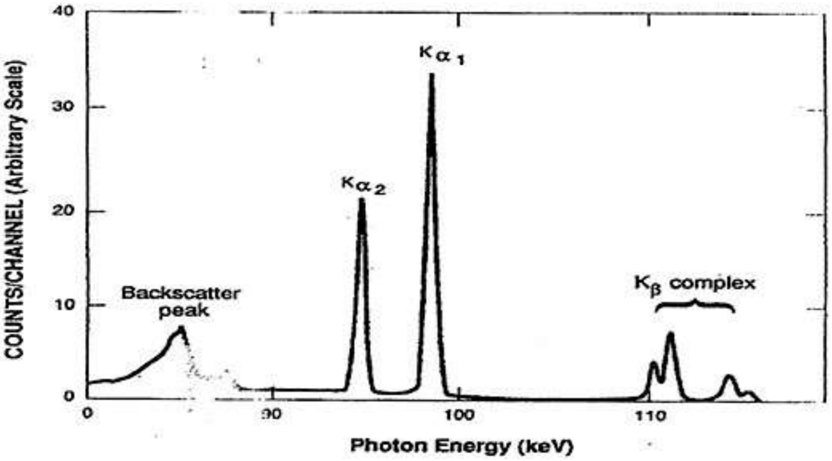

Figure (3.2) K x-ray spectrum of uranium, the excitation is ^{57}Co

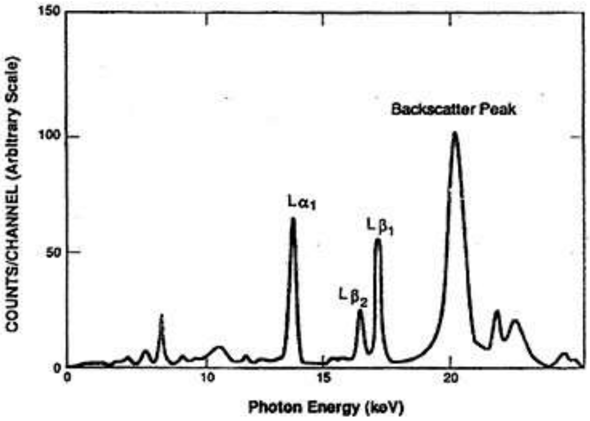

Figure (3.3) L x-ray spectrum of uranium. The excitation source is ^{109}Cd

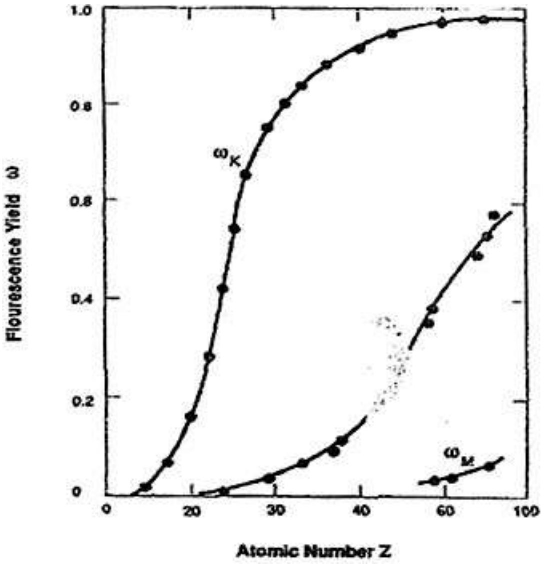

Figure (3.4) Fluorescence yield for K, L, and M x rays as a function of atomic number

Attenuation limits the sample size that can be analyzed by x-ray transmission techniques. In general, transmission techniques are amicable for samples whose transmission path lengths are less than four or five mean free paths [10].

Equation (3.2) is useful when comparing K XRF and L XRF. For L XRF, is larger and more of the excitation interacts with the sample. For K XRF, is smaller anti both the excitation photons andx rays are attenuated less (relative to L XRF). This attenuation difference imphes that L XRF is more sensitive (more

X-rays produced per unit excitation flux and cross-sectional area) than K XRF. On the other hand, K XRF allows greater flexibility with respect to the choice of sample container and intervening absorbers.

The choice of geometry is very important in an XRF system. Although photoelectric interactions of the excitation photons with analyze atoms are of primary interest, other interactions, particularly Compton backscatter interactions, must be considered. The energy of a Compton-scattered gamma ray is [10]:

$$E' = \frac{511}{(1-\cos\emptyset+\frac{511}{E})} \qquad (3.3)$$

Where: E' = scattered, incident photon energy in keV.
∅ = angle between incident and scattered pho tons.

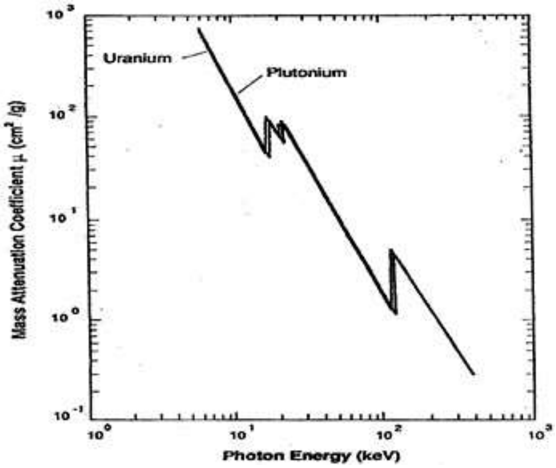

Figure (3.5) Mass attenuation coefficient vs. energy for uranium and plutonium

The energy E' is a minimum when (∅ = 180), and photons that have scattered at or near this angle can produce a back scatter peak in the measured spectrum. For 122-keV photons from ^{57}Co (a suitable source for K XRF of uranium or plutonium), the backscatter peak is k 82.6 keV. If the scattering angle ∅ is 90o, E' is 98.5 keV, which is in the middle a K x-ray spectrum from uranium and plutonium.

If ^{57}Co is used as an excitation source, the measurement geometry should be arranged such that is close to 180o for most of the scattered gamma rays that reach the detector. This arrangement puts the backscatter peak and the Compton continuum of scattered photons below the characteristic x rays and minimizes the background under the x-ray photo-peaks. The annular source described later in the chapter provides this favorable geometry. For L x rays, the geometry is not as critical because E'(180o) is 20.3 keV for 22-keV silver x rays from ^{109}Cd (a good L XRF source for uranium), and the backscatter peak is above the x-ray region of interest. Scattering materials near the detector must be carefully controlled to minimize the magnitude of the backscatter peak. Some investigators use excitation sources with energies much higher than the binding energy of interest, thereby minimizing the scattering effects in the spectral region of the induced x rays. This approach requires higher-intensity excitation sources (by an order of magnitude or more) in order to produce sufficient x-ray activity.

The detector must be shielded from the excitation source and other background radiation to reduce dead time and pileup losses. Detector collimation is usually necessary to limit the interference from unwanted sources. To stabilize the x-ray response, the relative positions of the source, sample, and detector must be fixed; often these components are physically connected. Figure 3.6 shows a possible geometry for a transmission-corrected XRF analysis [10].

3.3 Type of Sources

To excite atoms in the sample excitation source is needed. Two types of sources are commonly used: discrete gamma-ray or x-ray sources and continuous sources such as x-ray generators.

Each has advantages and disadvantages. The selection of a suitable source involves consideration of type, energy, and strength. It is most efficient to choose a source whose energy is above but as close as possible to the absorption edge of interest. As shown by the graph of vs. photon energy in Figure (3.6), the value of the mass attenuation coefficient is greatest just above an absorption edge [10].

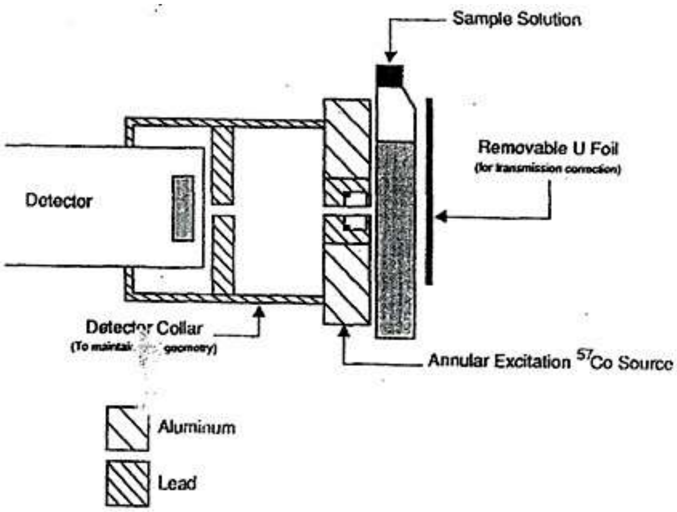

Figure (3.6) Cross-sectional view of geometry of excitation source, sample and detector

Cobalt-57 emits gamma ray at 122 keV, an efficient energy for K-shell ionization of either uranium or plutonium. X-ray generators are available for K XRF of uranium and plutonium, but they are too bulky for portable applications. A good discrete source for L XRF of uranium and plutonium is ^{109}Cd, which emits silver K x rays (energy 22 = keV). X-ray generators are available that are small enough for portable applications that require photons in the 25 keV energy range.

Discrete line sources are small, extremely stable, and operationally simple, making them attractive for many XRF applications. Their major disadvantage is that they decay with time and require periodic replacement (Two commonly used sources, ^{57}Co and ^{109}Cd, have half-lives of 272 days and 453 days, respectively.) Another disadvantage is that discrete sources cannot be turned off, causing transportation and handling difficulties. Because the source strength is often 1 mCi or greater, both personnel and detector must be carefully shielded.

Table (3-2) lists some radioisotopes that can be used for XRF analysis of uranium and plutonium. The geometry of the annular source showed. Figure (3.7) is commonly used because it shields the detector from the excitation score and minimizes backscatter interference [10].

Table (3.2) Excitation sources suitable for uranium and plutonium

			Useful Emissions	
Radionuclide	**Half-Life**	**Decay mode**	**Type**	**Energy (KeV)**
^{57}Co	270 d	Electron Capture	gamma rays	122
			gamma rays	136
^{109}Cd	-	Electron Capture	Ag K x rays	22
^{75}Se	-	Electron Capture	gamma rays	121
			gamma rays	136
^{144}Ce	-	beta decay	Pr K x rays	36
			gamma rays	134
^{125}I	-	Electron Capture	Te K x rays	27
			gamma rays	35
^{147}Pm-Al	-	beta decay	continuum	12-45[a]

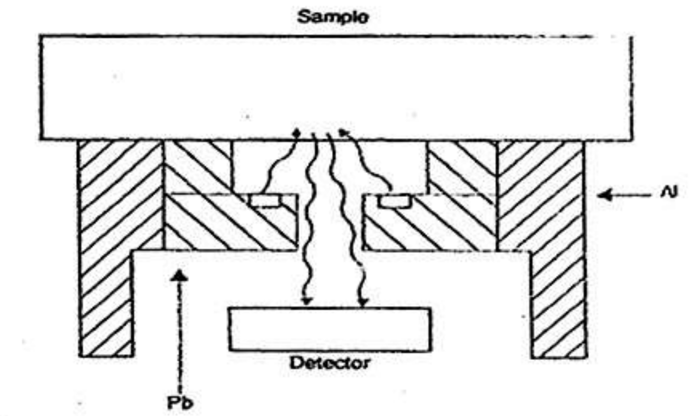

Figure (3.7) Annular excitation sources

X-ray generators produce bremsstrahlung by boiling electrons off a filament and accelerating them into a target. Because they require a high-voltage supply and a means of dissipating the heat produced in the target, x-ray generators can be bulky, especially for higher operating potentials. Small generators are available that operate below 70 keV, and portable generators, with power ratings up to 50 W, are available that do not require eliminate cooling systems. For a given power rating, higher maximum operating voltage achieved at the expense of lower available current.

The spectrum from an x-ray generator spans the energy range from the accelerating potential of the generator to the transmission cutoff of the x-ray window. The shape I (E) and total intensity (I) of this distribution is given by:

$$I(E) \propto Z(V - E)i \qquad (3.4)$$

$$I \propto ZV^2 i$$

Where:

i = tube current.

V = operating voltage.

Z = atomic number of target.

Figure (3.8) shows the .output spectrum from an x-ray generator. In addition to the continuous spectrum, the characteristic x rays of the target material are produced. These x rays may cause an interference, which can be removed with filters. The filter chosen should have an absorption edge just below the energy to be attenuated.

X-ray generators can be switched on and off, and their energy distribution and intensity can be varied as desired. They typically provide a more intense source of photons than radio isotopic sources (~10^{12} photons/s or greater). However, their flexibility is possible only at the expense of simplicity and compactness. Because an x-ray generator is an electrical device, system failures and maintenance problems are possible concerns. The assay precision is dictated by the stability of the x-ray tube. Modem generators exhibit less than 0.1% fluctuation for short-term stability and 0.2 to 0.3% for long-term stability [10].

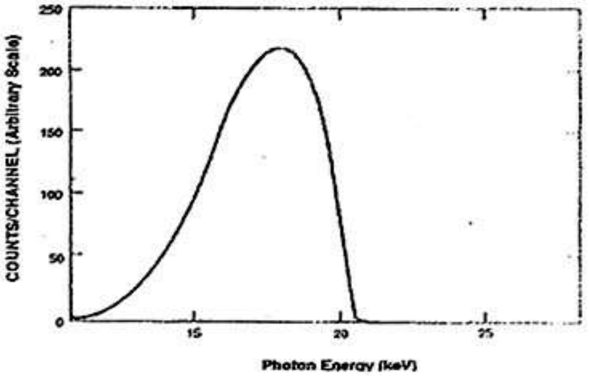

Figure (3.8) typical x-ray generator spectrums. The generator target is tungsten and the operating potential is 20.4 kV.

Other sources may be used for XRF. A secondary fluorescent source uses a primary photon source to excite the characteristic x rays of a target, and the target x rays are used to excite the sample to be analyzed. The primary excitation source can be discrete or continuous. This scheme can produce a great variety of monoenergetic excitation photons, depending on the target material. The major drawback is the need for a high-intensity primary source. If the primary source is a radioisotope, radiation safety may be an important concern. It is possible to make a bremsstrahlung source using a radioisotope rather than an x-ray generator. Such a source consists of a beta-decaying isotope mixed with a target material (for example, ^{147}Pm-Al, with aluminum being the target material).

3.4 XRF Spectrometers

There are two types of XRF spectrometer. One is called wave length dispersive (WDXRF) and the other is called energy dispersive (EDXRF). In the (WDXRF) spectrometer the tube irradiates a sample and the radiation coming from the sample is detected. The detection system is however different from EDXRF spectrometer.

For (WDXRF), the detection system is a set of collimators, a diffraction crystal and a detector. The X-rays coming from the sample fall on the crystal, and the crystal diffracts (reflects) the X-rays with different wavelengths (energies) in different directions, (this is equivalent to a prism that separates white light into all the different colors).

Different types of detectors are used in XRF. EDXRF mainly uses solid-state detectors where WDXRF uses gas-filled detectors and scintillation detectors [10].

The EDXRF detector is a wide-range detector and measures all elements from Na up to U. Gas-filled detectors measure element from Be up to Cu and the scintillation detector from Cu up to U. All these detectors produce an electrical pulse when an X-ray photon enters the detector, and the height of this pulse is proportional to the energy of the incoming photon. The pulses are amplified and then counted by a multi-channel analyzer.

There are three important properties of detection systems. Resolution, sensitivity and dispersion, Resolution is the ability of the detector to distinguish between many different energies, Sensitivity indicates how efficiently incoming photons are counted. If for instance a detector is very thin, incoming photons may pass it without producing a pulse. Sensitivity is high if the ratio of the number of pulses against the number of incoming photons is high. Dispersion indicates the ability of the detector to separate X-rays with different energies. A high dispersion means that different energies are separated well.

3.4.1 Multi-channel analyzer (MCA)

The MCA counts how many pulses are generated in each height interval. The number of pulses of a certain height gives the intensity of the corresponding energy. The ability of the detector and MCA to distinguish between different energies is called the resolution.

3.4.2 ED solid-state detector

Figure (3.9) shows the basic design of a solid-state detector. It is constructed with body of silicon, germanium or other semiconducting material. A beryllium window allows X-ray photons to enter the detector. On the front there is a dead layer and on the back there is a collecting plate [10].

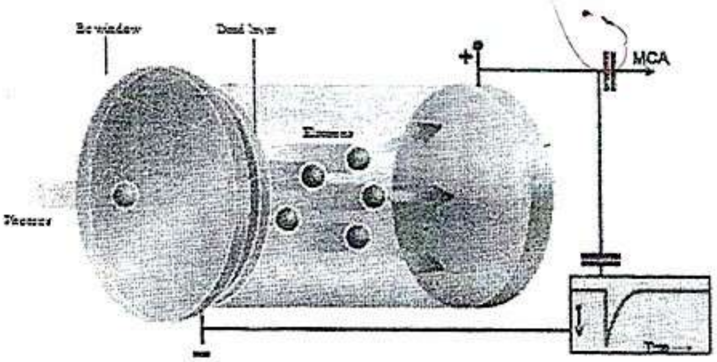

Figure (3.9) Basic design of a solid-state detector

3.4.3 Gas-filled detector

A gas-filled detector, It is constructed from a metal (often aluminum) cylinder at earth potential with a co-axial 50 mm tungsten anode wire running downs its length. The anode wire is raised to a high voltage (1300 - 2000 V). a beryllium entrance window allows X-ray photons to enter the detector, which is filled with an inert counting gas (Ne, Ar, Kr or Xe, and occasionally He).

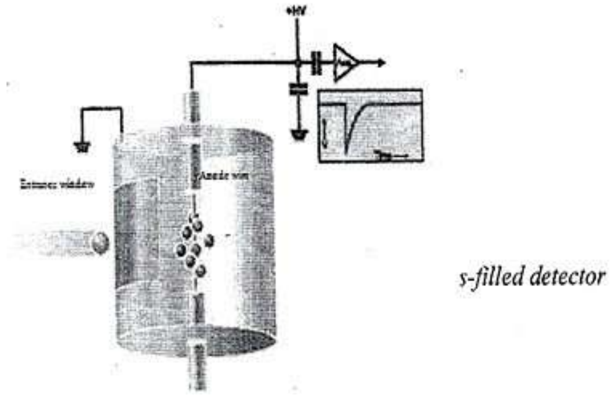

Figure (3.10) Gas filled detector

3.4.4 Scintillation detector

The basic design of a scintillation detector, It consists of four main parts: a beryllium window, Nal scintillates crystal and a photo multiplier tube with Sb/Cs photo cathode.

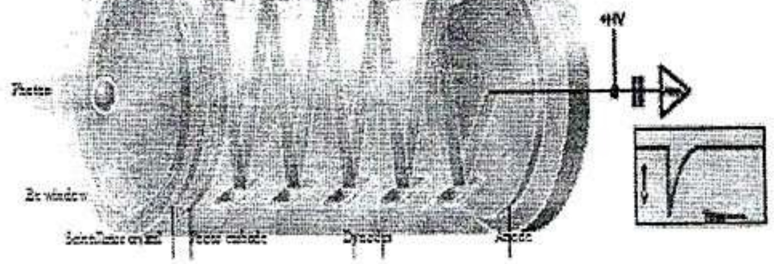

Figure (3.11) Basic design of a scintillation detector

3.5 Correction for Sample Attenuation

Sample attenuation is a fundamental limitation to the accuracy of XRF analysis. Attenuation corrections are required for the x-rays leaving the sample and also for the gamma rays or x-rays from the excitation source. X-ray fluorescence analysis is unsuitable for large, solid samples, because the attenuation is too large to be accurately treated with any correction procedure. For example, the mean free path of 122-keV gamma rays in uranium metal is approximately 0.013 cm. The low penetrability of this radiation means that XRF can be accurately used only if the sample is smooth and homogeneous. This limitation is even truer for L XRF using 22-keV photons. X-ray fluorescence can be used to accurately assay dilute uranium solutions because the mean free path of photons in water is approximately 6.4 cm at 122 keV and 1.7 cm at 22 keV. Because the excitation source energy is above the absorption edge and the energies of the characteristic x-rays are just below the absorption edge, the attestation of the excitation radiation is higher and determines the range of sample thickness that can be accurately assayed. Figure 10.12 plots the mean free path of 122-keV gamma rays as a function of uranium concentration (uranyl nitrate in 4-M nitric acid).

For quantitative analysis, the x-ray emission rate must be related to the element concentration. The desired relation is:

$$\rho = \frac{\mathrm{RR} \times \mathrm{CF(RL)} \times \mathrm{CF(AT)}}{\mathrm{K}} \tag{3.5}$$

Where: ? ? = element concentration.

RR = raw rate of x-ray detection.

CF(RL) = correction factor for rate-related losses.

CF(AT) = correction factor for attenuation.

K = calibration constant.

CF(RL) can be determined using either pulser or radioisotope normalization . The attenuation correction has two parts; one for excitation radiation and one for fill reseed x rays.

Consider a far-field measurement geometry where the sample is approximated by a slab and the excitation source is mono-energetic (see Figure (3.12). The flux F_γ of excitation photons at a depth x in the sample is given by:

$$F_\gamma = I_\gamma \exp(-\mu^\gamma X/\cos\varnothing) \tag{3.6}$$

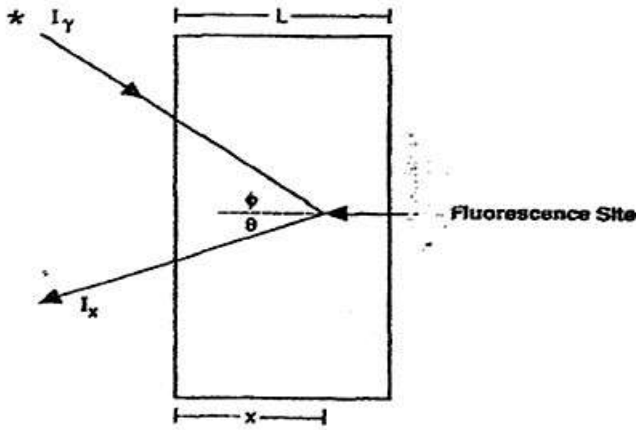

Figure (3.12) General XRF slab geometry

The variables in Equation (3-6) through (3-10) are defined in Table (3-3). The number of excitation photon that interacts in the volume dx and create $K_{\alpha 1}$ x ray is:

$$F_x dx = F_\gamma T \rho \omega B \frac{dx}{\cos\varnothing} \tag{3.7}$$

The fluoresced x ray are attenuated in the sample according to:

$$F_x(\text{out}) = F_x \exp(-\mu^x X/\cos\theta \tag{3.8}$$

Combining and integrating Equations (3-6) through (3-8) yields the following expression for the x-ray rate at the detector surface:

$$I_x = \frac{I\gamma T\rho\omega B\Omega}{4\pi[(\cos\theta/\cos\phi)\mu^{\gamma} + \mu^{x}]}\left\{1 - \exp\left[-\left(\frac{\mu^{\gamma}}{\cos\phi} + \frac{\mu^{x}}{\cos\theta}\right)L\right]\right\} \quad (3.9)$$

The factor $(\Omega/4\pi)\cos\phi/\cos\theta$ has been added for normalization. If x-ray generator is used as the excitation source Equation 3-9 must be integrated from the absorption edge to the maximum energy of the generator.

When the sample is infinite lythick for the radiation of interest, Equation (3.9) becomes:

$$I_x = \frac{I\gamma T\rho\omega B\Omega}{4\pi[(\cos\theta/\cos\phi)\mu^{\gamma} + \mu^{x}]} \quad (3.10)$$

This equation is similar to that of the enrichment meter. The result is very important for XRF analysis because it implies that the x-ray rate is directly proportional to the concentration of the fluoresced element.

In plutonium and high a enriched uranium materials, the self-excitation of x rays by the passive gamma rays can complicate the assay. For mixed uranium/plutonium materials, the dominant signals are passive x rays from the alpha decay of plutonium. When the excitation source can fluoresceplutoniumand uranium (as can 57Co and 109Cd), additional uranium fluorescence is caused by the plutonium x rays. A separate passive count is usually required to correct for this interference.

Table (3.3) Variables in Equations 3.6 through 3.10

I_0	excitation flux at sample surface
τ	photoelectric cross section, K shell, energy
? ?	concentration of elements
ω	K fluorescence yield
B	branching ratio for
Ω	detector solid angle
$\mu^{\gamma} = \sum \mu_i^{\gamma} \rho_i$	linear attenuation coefficient, energy, element i
$\mu^{x} = \sum \mu_i^{\gamma} \rho_i$	linear attenuation coefficient, x energy, element i
ϕ	incident angle of excitation
θ	exiting angle of x ray
L	slab thickness

The most effective XRF methods account for sample attenuation. The method is effective only if the standards are well characterized, match the samples chemically. A procedure that is less sensitive to matrix variation is the transmission-corrected assay in which a transmission measurement is made for each sample to correct for attenuation. Consider the attenuation correction factor for the situation show by assuming = 0). The expression for CF(AT) has the functional form for a slab that was :

$$\mathrm{CF(AT)} = \frac{-\,\mathrm{In}\,\alpha}{1-\alpha} \qquad (3.11)$$

Where:

$$\alpha = \exp\left[\left(\frac{\mu^{\gamma}}{\cos\phi} + \right) L\right]$$

A measurement of the transmissions of the excitation and the fluoresced x rays can be used to determine. For this method, a foil of die element being measured is placed behind the sample and the induced x-ray signal is measured with and without the sample. An additional measurement is made with the sample only (no foil), and is computed from:

$$\alpha = \frac{I_{T} - I_{S}}{I_0} \qquad (3.12)$$

Where: I_T = fluoresced x-ray intensity with foil plus sample.
I_S = fluoresced x-ray intensity with sample only.
I_0 = fluoresced x-ray intensity with foil only.

This measurement includes the attenuation of the excitation source and of the induced x-ray signal. Although there are advantages to using the same element in the transmission foil as that being assayed, other elements can be used if their characteristic x rays are sufficiently close to those of the assay element. For example, thorium metal has been used successfully for the measurement of uranium solutions.

A suitable number of standards is needed to evaluate the calibration constant K in Equation (3.5). Equations (3-11) and (3-12) are exact only for far-field geometry, and most XRF measurements are made in near-field geometry. Therefore, even with rate and sample attenuation corrections, it is important to use several standards to evaluate the calibration constant K [10].

3.6 XRF analysis

Qualitative analysis determines which elements are present and quantitative their net intensities from the measured. The net intensities are used in the quantitative analysis to calculate the concentrations of the elements present.

(EDXRF) and (WDXRF) often use slightly different methods for qualitative analysis. In EDXRF the area of a peak gives the intensity while in (WDXRF) the height of the peak gives the intensity. Both methods would work for (EDXRF) and (WDXRF), but both have their specific advantages and disadvantages.

3.6.1 Qualitative analysis in (EDXRF)

The first step in the analysis is to determine the top positions and the areas of the line profiles. The positions of the tops represent the presence of elements and the areas represent the intensities of the lines.

Peak search and peak match are used to find which elements are present in the sample. Peak search uses a mathematical technique to find the peaks in a spectrum. Peak match determines the elements to which the peak profiles belong. This is done by comparing the positions of the peaks to a database holding the positions of all possible lines.

3.6.2 Qualitative analysis in (WDXRF)

As with EDXRF, peak search and peak match are used to discover which elements are present in the sample. One again, peak search finds the peaks, and peak match determines the associated elements by referring to a database [11]. Measuring peak height and background subtraction in WDXRF it is common practice to measure the intensity at the peak of a line and at a few background positions close to the peak. The positions must be chosen carefully and must avoid other peaks. The background under the peak is determined by interpolating the intensities measured at the background positions.

3.6.3 Counting statistics and detection limits

The detector counts incoming photons to detect a peak of an element; it must be significantly above the noise (variation) in the background. The noise depends on the number of X-ray photons counted. The lower the number of photons counted, the higher the noise. The analysis is commonly based on the number of photons counted per second, but as above, the noise depends on the total number of photons counted. By measuring for a longer period, it is possible to collect more photons and hence reduce the noise [11].

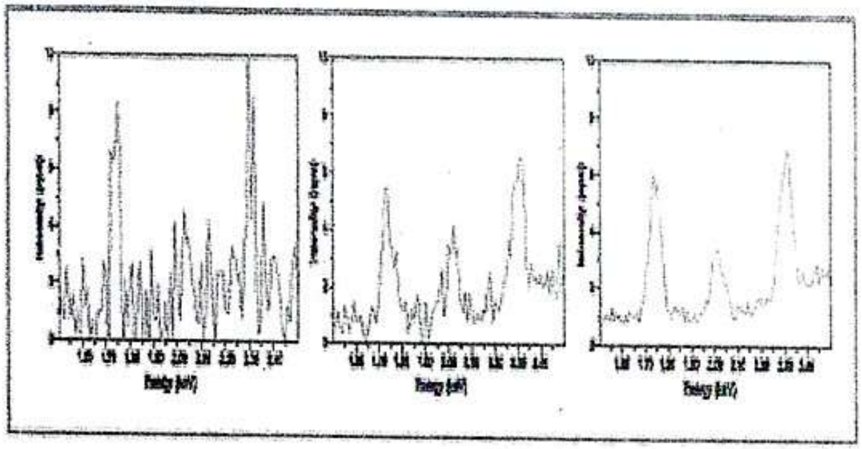

Figure (3.13) Spectra measured over different times

Figure3.13 shows three spectra of the same material, but with different measurement times. In the first spectrum it is difficult to determine the peaks and their heights.

In the second, the peaks are more prominent and in the third they can be clearly seen and their net heights can be determined accurately.

A commonly accepted definition for the detection limit is that the net intensity of a peak must be 3 times higher than the standard deviation of the background noise.

The standard deviation of the background noise equals the square root of the intensity (in counts), so elements are said to be detectable if:

$$C_t = D_t + E_t - R_t - [1 + \text{corrections}] \qquad (3.13)$$

C_t= standard deviation from sample concentration.

D_t= standard deviation from sample measurement (counts).

R_t = standard deviation from sample standard measurement (counts).

[1 + corrections] = M_i= Matrix correction factor.

t = Time.

3.6.4 Quantitative analysis in (EDXRF) and (WDXRF)

Quantitative analysis is basically the same for EDXRF and WDXRF. The only difference is that in EDXRF the area of a peak gives the intensity, while in WDXRF the height of a peak gives the intensity. The exact same mathematical methods can used to calculate the composition of samples. In quantitative analysis, the net intensities are converted into concentrations. The usual procedure is to calibrate the spectrometer by measuring one or more reference materials. The calibration determines the relationship between the concentrations of elements and the intensity of the fluorescent lines of those elements. Unknown concentrations can be determined once the relationship is known. The intensities of the elements with unknown concentration are measured, with the corresponding concentration being determined from the calibration.

3.6.5 Matrix effects and matrix correction models

Ideally, the intensity of an analytical line is linearly proportional to the concentration of the analyst and it also depends on the presence and concentrations of other elements. These other elements can lead to attenuation or to enhancement [11].

Matrix correction models use terms to correct for the absorption and enhancement effects of the other elements. This is done in various ways, but they all, in one way.

$$C_i = D_i + E_i - R_i - M_i \tag{3.14}$$

Or $$C_i = (D_i + E_i - R_i) - M_i \tag{3.15}$$

The first equation, but the method is also applicable to the second equation. M is the matrix correction factor, and the difference between the models lies in the way they define and calculate M. The corrections are numeric values depending on the concentrations and/or intensities of the matrix elements. Many people have suggested ways to define and model the corrections, and models are commonly named after the person (s) who proposed them.

3.6.6 Fundamental Parameter (FP) matrix correction models

Sherman derived the mathematical equations that describe the relationship between the intensity of an element and the composition of a sample. This equation contains many physical constants and parameters that are called Fundamental Parameters. The Sherman equation is used to calculate the values of the matrix correction M gully by theory and the model becomes [11]:

$$C_i = D_i + E_i - R_i - M_i \tag{3.16}$$

At least two standards are required to calculate D and E, or just one if only E has to be calculated. M is calculated for each individual standard, and the factors D and E are determined for all elements.

The matrix factors M can only be calculated accurately if the full matrix is known, because all absorption and enhancements have to be taken into account. The calculations are quite complicated because FP accounts for all effects; it can be used over virtually the full concentration range and for all types of samples as long as the majors are known.

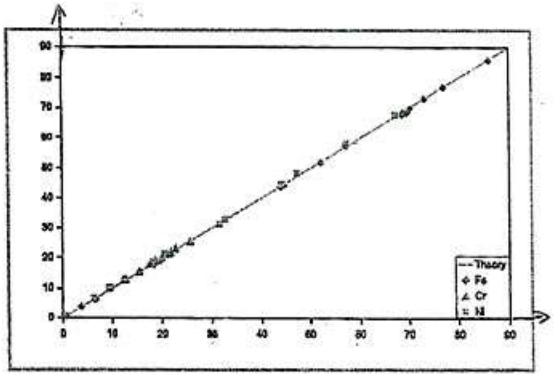

Figure (3.14) shows the results using the same FP calibration for samples with a very wide concentration range.

3.6.7 Compton matrix correction models

The Compton method is an empirical one. The intensity of a Compton scattered line depends on the composition of the sample. Light elements give high Compton scatter, and heavy elements low Compton scatter, which is used to compensate for the influence of the matrix. The model is:

$$C_i = D_i + E_i \cdot \frac{R_i}{R_c} \qquad (3.17)$$

The Compton line can be a scattered tube line, or a line originating from a secondary target id 3D optics is used.

3.6.8 Line overlaps correction

The fractions were determined by measuring dedicated standards. Another method is to determine the overlap factors by regression. The calibration model is extended with terms that describe the line overlap [11]:

$$C_i = D_i + E_i \cdot \left(R_i - \sum_{\substack{overlapping \\ lines\ j}} f_{ij} \, . R_j \right) . M_i \qquad (3.18)$$

The overlap factors f_{ij} are determined by regression. The problem with this equation is that it can be non-linear, which makes it difficult to calculate the factors. If the calibration is limited to a small range, and when the variation in M is small, it can be approximated by:

$$C_i = D_i - R_i - \sum_{\substack{overlapping \\ lines\ j}} f_{ij} \cdot R_j \cdot M_i \qquad (3.19)$$

This is a linear equation, and it is mathematically easy to calculate the overlap factors f_{ij} and the other calibration parameters simultaneously.

These methods require that the overlapping intestates be measured. In EDXRF this is not a problem because the whole spectrum is generally measured.

In WDXRF, often only the lines of the elements of interest are measured and not the overlapping lines. The intensity of the overlapping lines is, over a limited range, proportional to the concentration of the originating element. The following equation can therefore be used[11]:

$$C_i = D_i - \sum_{\substack{overlapping \\ lines\ j}} f_{ij} \cdot R_j \cdot M_i \qquad (3.20)$$

3.7 Thin and layered samples

Thin samples require special treatment. For thick sample, the intensity corrected for matrix effects is linearly proportional to the concentration and does not depend on the thickness of the sample. This is because only radiation coming from a layer close to the surface can leave the sample and reach the detector. Radiation coming from deeper layers is not detected, and making the sample thicker will have no effect on the measured intensity.

The situation is different for thin samples. As long radiation from the bottom of the sample can still pass through the sample and reach the detector, it will affect the measured intensity. If the measured intensity of a thin sample is lower than the intensity of a standard, it is not possible to tell whether the concentration of the analytic lowers or whether the sample is thinner than the standard.

The Compton correction model will correct for finite thickness. The Compton line and the analytical line approximately have the same thickness dependency. By dividing the intensity of the analytical line by the intensity of the Compton line the thickness dependency vanishes.

If the thickness of the sample is known, it can be taken into account in the Fundamental Parameter calculations and it again becomes possible to calculate the concentration of the analytic.

With Fundamental Parameters it is even possible to calculate the thickness and composition of layered samples and coatings. Examples are optical coatings, magnetic recording materials, semiconductor wafers. The Fundamental Parameters method stats with an initial guess of the thickness and composition and iteratively change the thickness and composition until the observed intensities are equal to the predicted intensities [11].

Analysis uses the same equations as used for the calibration. In the calibration, the D, E and correction factors are the parameters that have to be determined. The concentrations are known because standard with known composition were used. In the analysis, the opposite is true. The D, E and correction factors are known, and the concentrations are the unknowns that have to be determined. Often this is done by iterative methods.

The process starts with an initial guess at the concentrations, and these Concentrations are substituted in the right hand side of the equations. This gives new values for the concentrations that are substituted in the right-hand sides, again giving new values for the concentrations. This process is repeated until the concentrations converge to limiting values. The result of the final iterations is assumed to be the composition of the sample.

3.8 EDX-7000/8000 Energy-Dispersive X-ray

Fluorescence Spectrometers

The EDX-7000/8000 series of energy dispersive X-ray fluorescence spectrometers, incorporating a new high-performance semiconductor detector, provide excellent sensitivity, resolution, and throughput for an array of applications, from general screening analysis to advanced materials research in such fields as petrochemicals, chemicals, agriculture, and environmental See fig (3.15).

Figure (3.15) EDX-7000/8000Energy-Dispersive X-ray

Chapter Four

Analysis of Toys

4.1 Introduction

Energy dispersive X-Ray spectrometer (EDX) at (SSMO) in Khartoum Sudan and Portable X- Ray Fluorescence (XRF), in Sudan Customs were, used to analyze some toys. The analysis was made during the period 14/2/2018.

In this chapter concerned with display the concentration and determine elements content on toys.

4.2 Material and Instruments

The materials are toy samples and the instruments include (EDX) and (Portable XRF).

4.2.1 Samples

Toy samples in the form of different origin (china-Taiwan):-

1) Toys from China (11 samples)
2) Toys from Taiwan (10 samples)

4.2.2 Instruments

1) (EDX): energy dispersive x-ray with the following specifications was used to display the spectrum of each sample.

NAME:	EDX-spectrometer
TYPE:	EDX 7000/8000
MODEL:	EDX8000
COUNTRY OF ORIGIN:	Japan

2) Portable (XRF): portable x-ray fluorescence with following specification was used to display the concentration and determining elemental of each sample.

NAME:	Portable XRF

NUMBER: 505091

MODEL: X-MET5000

TYPE: XMDS2654

COUNTRY OF ORIGIN: Finland

4.3 Experimental procedures

a) Each sample is exposed to EDX for few minutes and the spectrum of each sample is displayed on the screen. The table of concentration of elements in the sample is printed.

b) Each sample is exposed to Portable XRF for few minutes but this devise cannot register any result. The sensitivity of the equipment is not suitable for such measurements. Therefore it will not be discussed further.

4.4 Results

4.4.1 Toys from China

By using (EDX):

Table (4.1) showing elemental concentration by using (EDX)

NO.	Cd		Pb		Hg		Cr		Sb	
	Ppm	3sigma	ppm	3sigma	ppm	3sigma	ppm	3sigma	ppm	3sigma
1	0.0	12.3	50.8	11.7	0.0	2.7	12.1	9.3	54.5	32.4
2	0.0	12.9	42.4	12.0	0.0	3.6	15.0	9.9	0.0	35.1
3	0.0	10.5	65.5	7.8	0.0	1.8	17.4	7.8	76.6	35.1
4	13.8	6.0	23.3	6.9	0.0	2.7	18.1	11.1	831.5	49.5
5	49.7	22.8	157.1	15.9	0.0	3.0	27.0	7.5	49.8	29.1
6	15.4	5.7	20.7	6.9	0.0	3.0	14.4	11.1	829.0	50.4
7	37.7	14.7	157.0	15.3	0.0	2.7	39.3	8.1	66.2	27.6

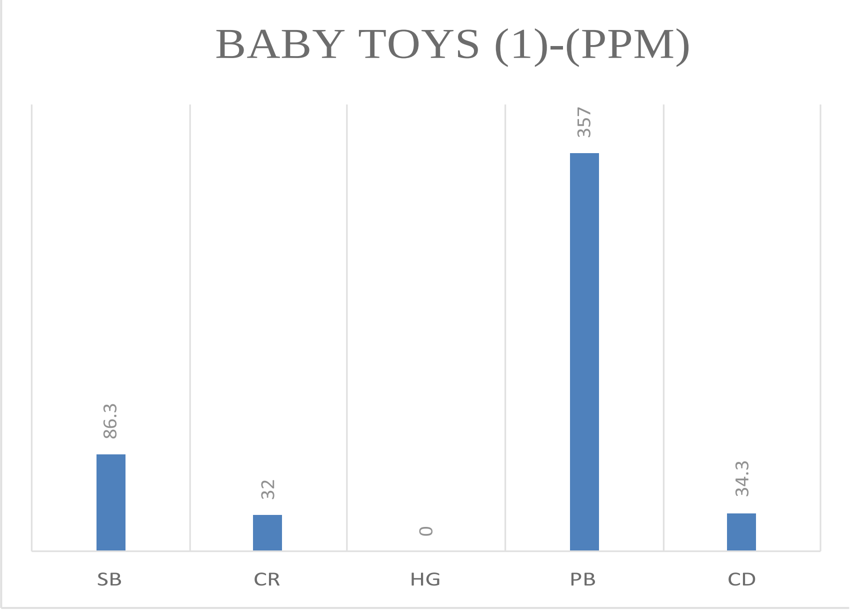

Figure (4.1.1) Baby Toys Number one concentration per PPM versus elements contained

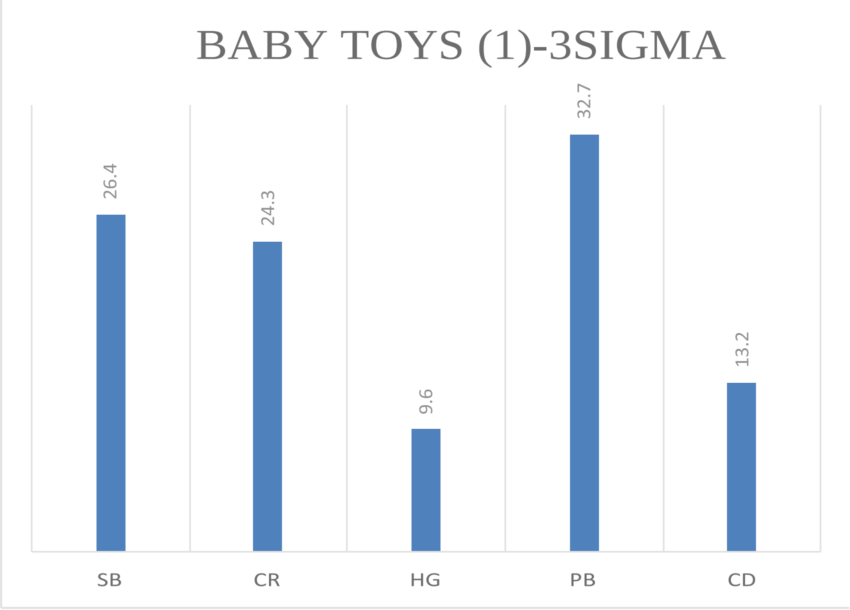

Figure (4.1.2) Baby Toys Number one concentration per3signma versus elements contained

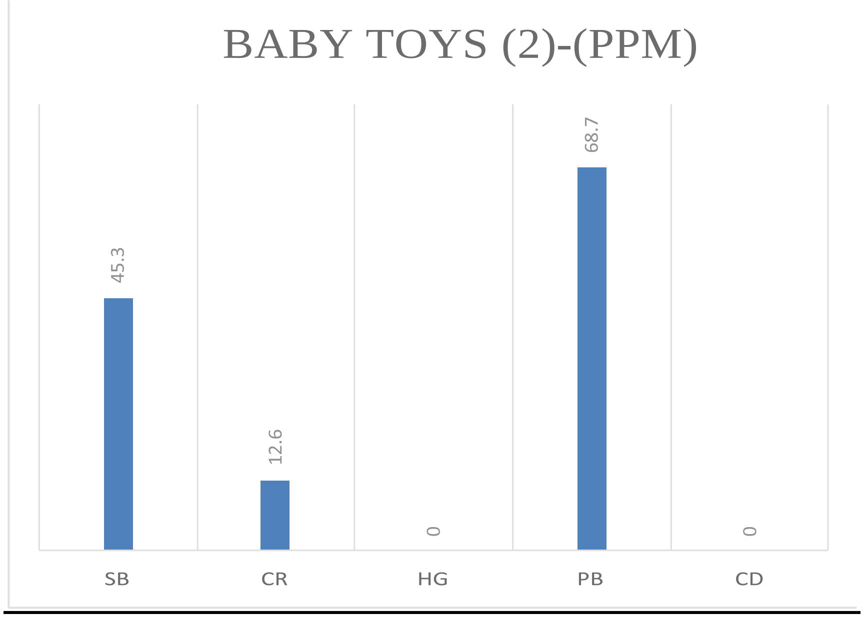

Figure (4.1.3) Baby Toys Number two concentrations per PPM versus elements contained

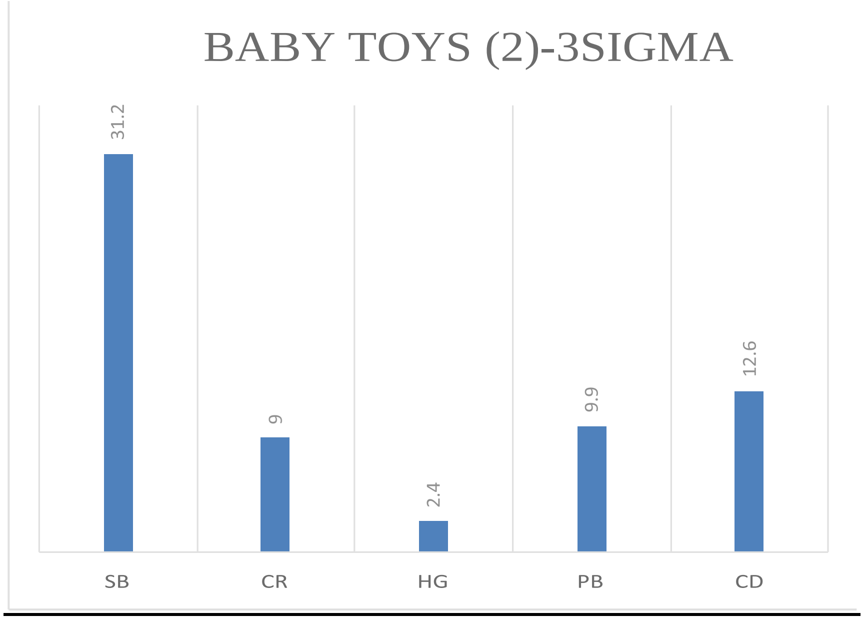

Figure (4.1.4) Baby Toys Number two concentration per3signma versus elements contained

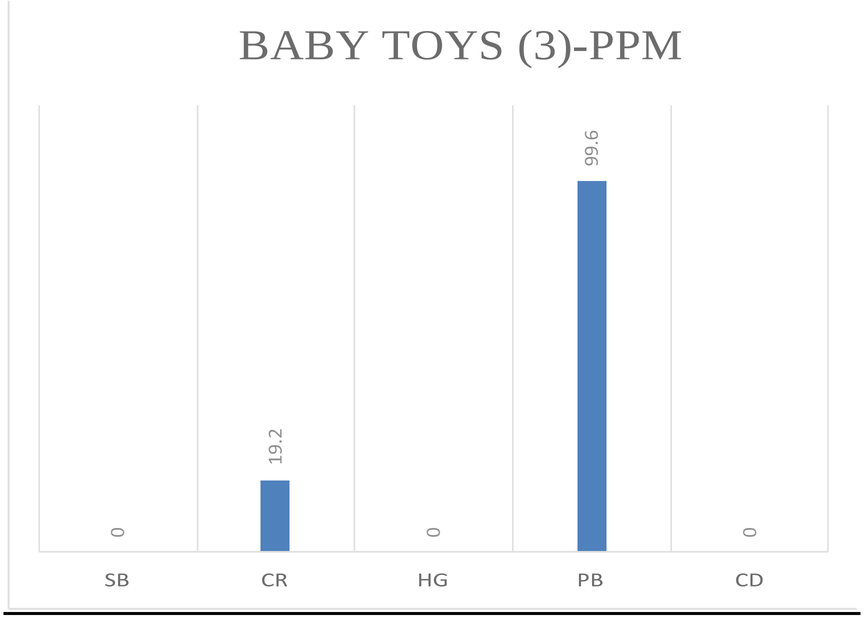

Figure (4.1.5) Baby Toys Number three concentrations per PPM versus elements contained

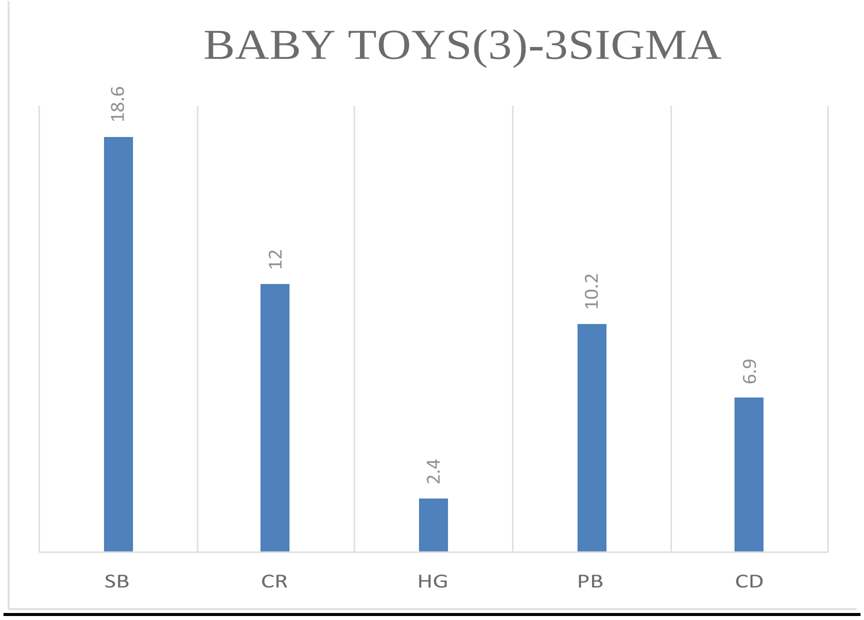

Figure (4.1.6) Baby Toys Number three concentration per3signma versus elements contained

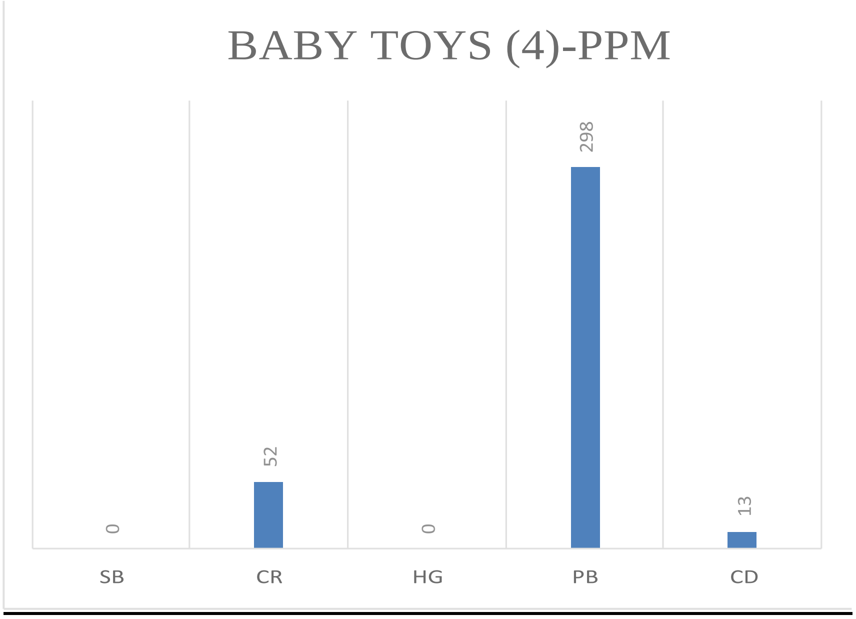

Figure (4.1.7) Baby Toys Number four concentrations per PPM versus elements contained

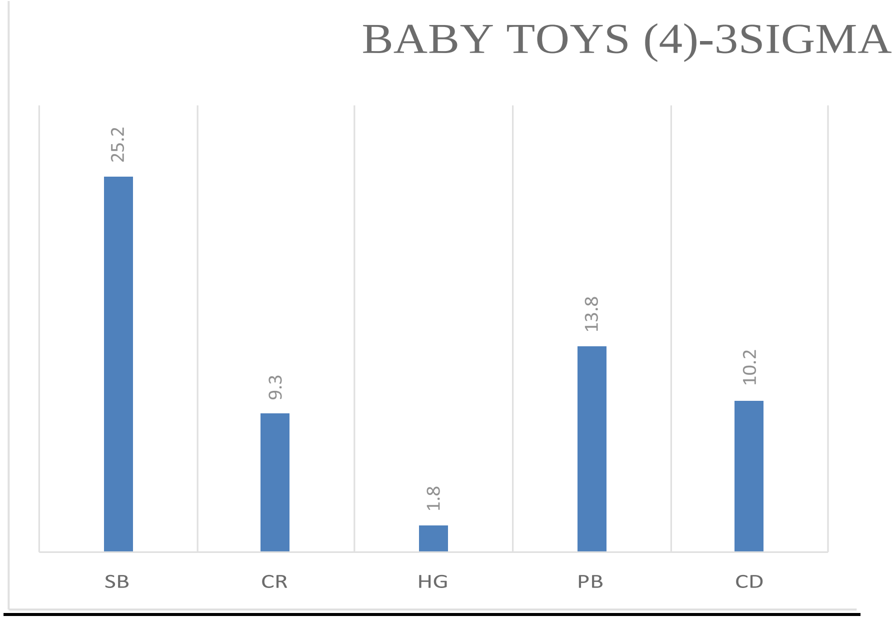

Figure (4.1.8) Baby Toys Number four concentration per3signma versus elements contained

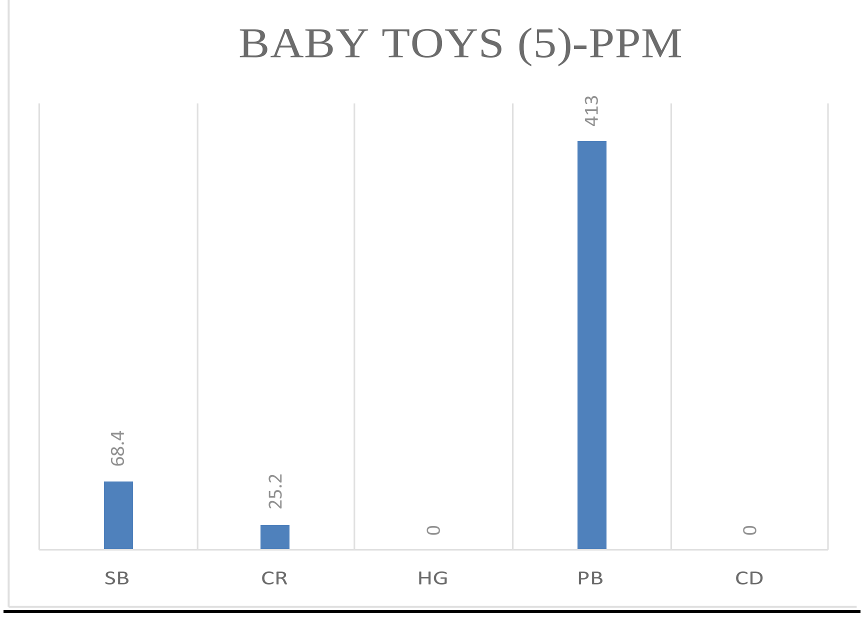

Figure (4.1.9) Baby Toys Number five concentrations per PPM versus elements contained

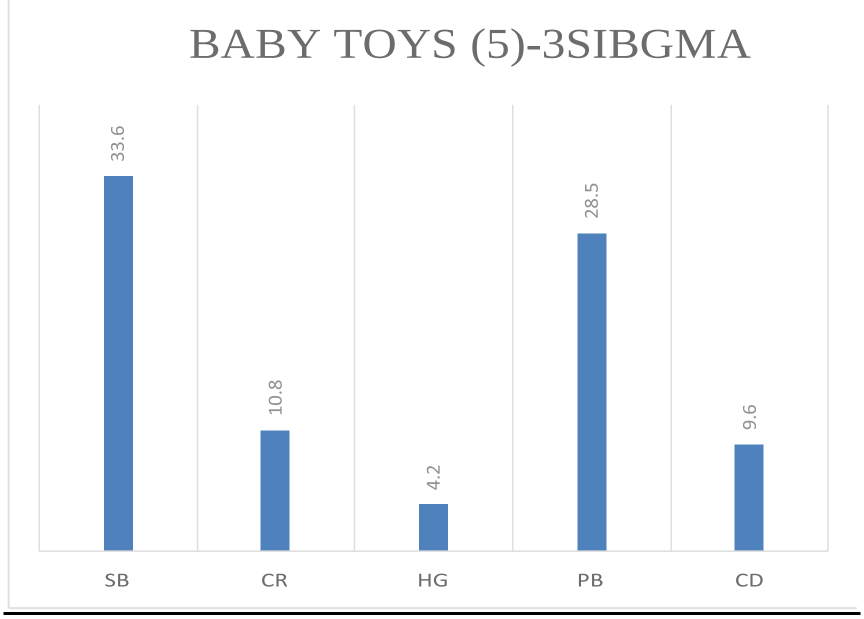

Figure (4.1.10) Baby Toys Number five concentration per3signma versus elements contained

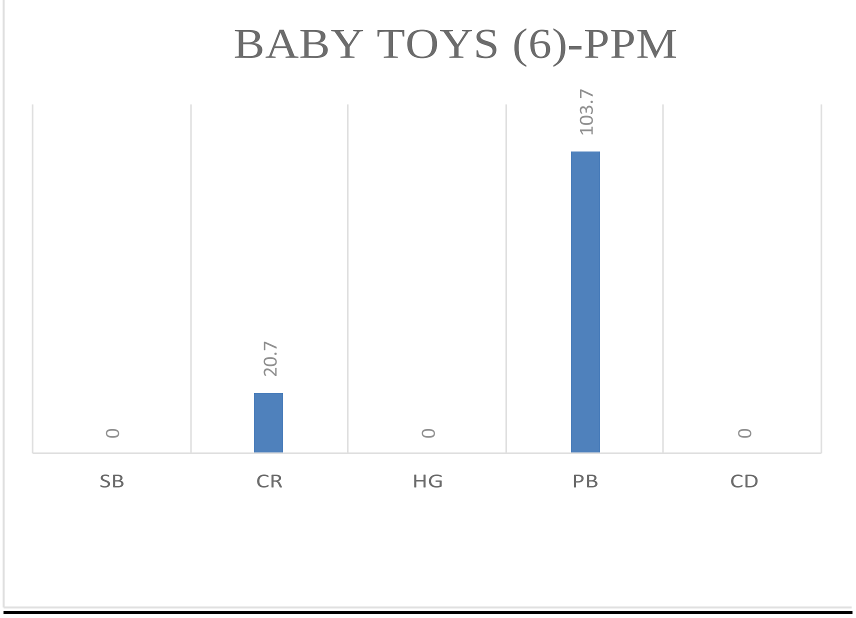

Figure (4.1.11) Baby Toys Number six concentrations per PPM versus elements contained

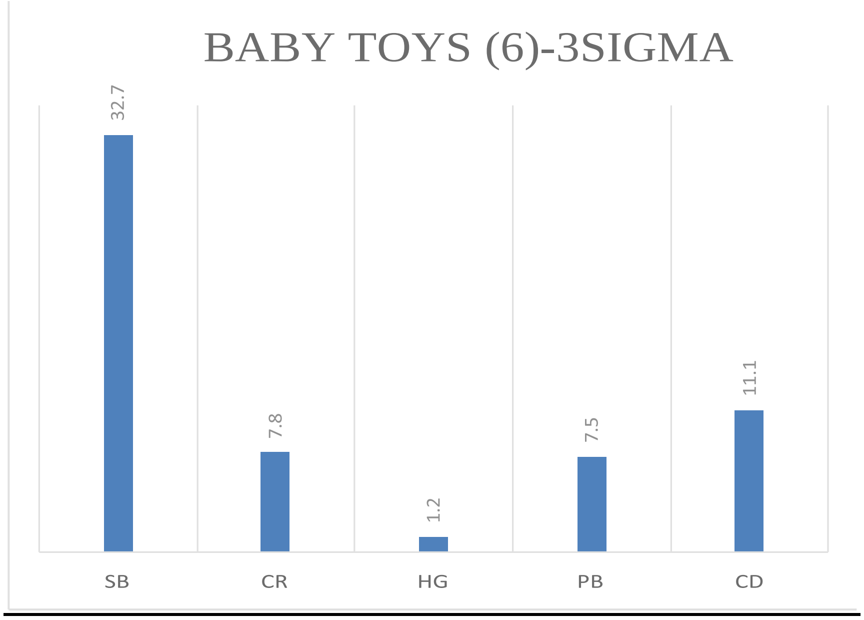

Figure (4.1.12) Baby Toys Number six concentration per3signma versus elements contained

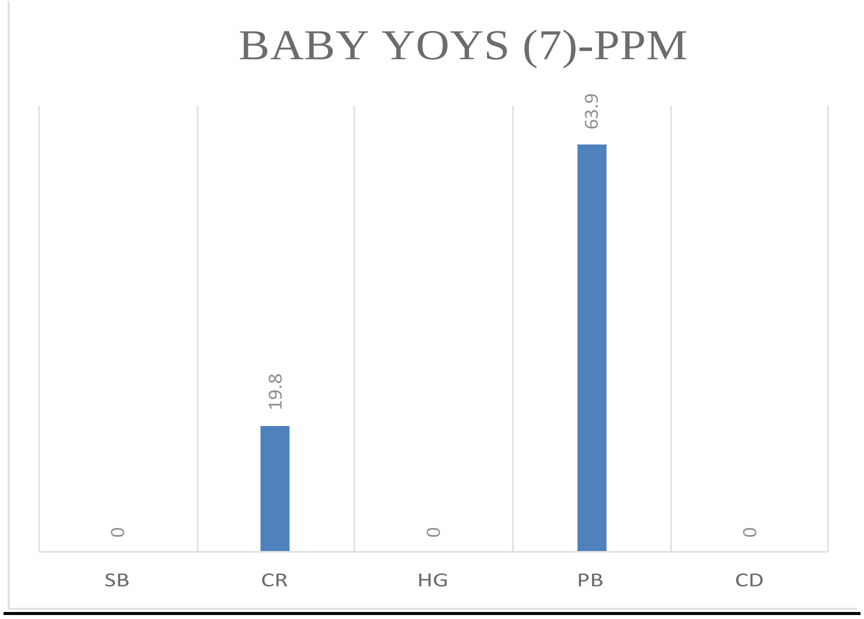

Figure (4.1.13) Baby Toys Number seven concentrations per PPM versus elements contained

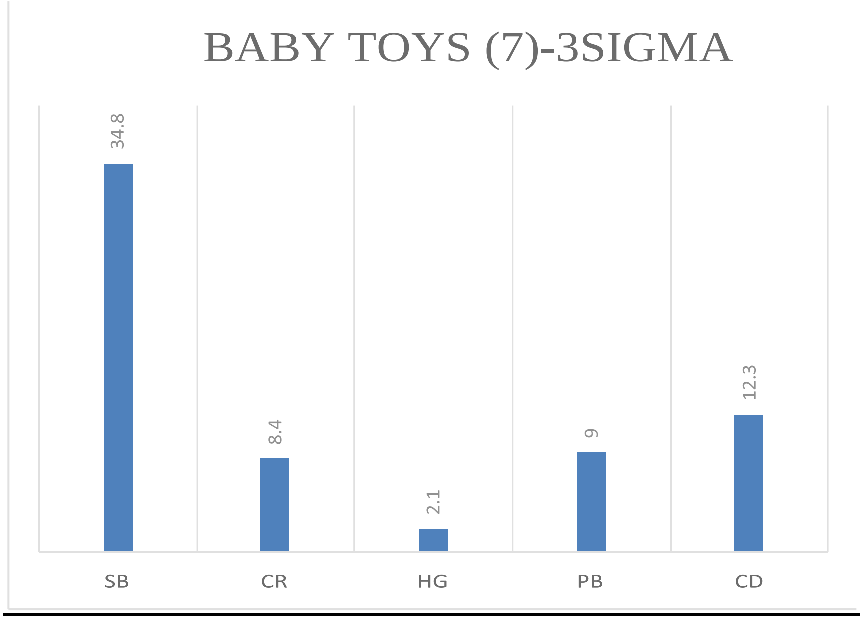

Figure (4.1.14) Baby Toys Number seven concentration per3signma versus elements contained

By using Portable (XRF):

NO RESULT

4.4.2 Toys from Taiwan

By using (EDX):

Table (4.2) showing elemental concentration By using (EDX)

NO.	Cd		Pb		Hg		Cr		Sb	
	ppm	3sigma	ppm	3sigma	ppm	3sigma	ppm	3sigma	ppm	3sigma
8	34.3	13.2	357	32.7	0.0	9.6	32.0	24.3	86.3	26.4
9	0.0	12.6	68.7	9.9	0.0	2.4	16.2	9.0	45.3	31.2
10	0.0	6.9	99.6	10.2	0.0	2.4	19.2	12.0	0.0	18.6
11	13.0	10.2	298.6	13.8	0.0	1.8	52.0	9.3	0.0	25.2
12	0.0	9.6	413.9	28.5	0.0	4.2	25.2	10.8	68.4	33.6
13	0.0	11.1	103.7	7.5	0.0	1.2	20.7	7.8	0.0	32.7
14	0.0	12.3	63.9	9.0	0.0	2.1	19.8	8.4	0.0	34.8
15	0.0	13.5	216.8	15.6	0.0	2.7	47.5	7.8	0.0	36.9
16	0.0	11.4	19.6	7.8	0.0	2.4	0.0	9.6	0.0	36.6
17	0.0	9.9	0.0	4.5	0.0	4.5	17.8	22.2	0.0	35.7
18	0.0	10.2	72.6	8.4	0.0	2.4	11.6	8.7	95.7	32.1
19	0.0	11.4	69.3	9.0	0.0	2.7	20.9	8.7	115.8	38.7
20	0.0	10.2	3.3	3.6	0.0	3.6	19.7	22.2	0.0	35.1
21	0.0	11.7	15.7	5.7	0.0	2.1	0.0	9.0	138.6	39.6

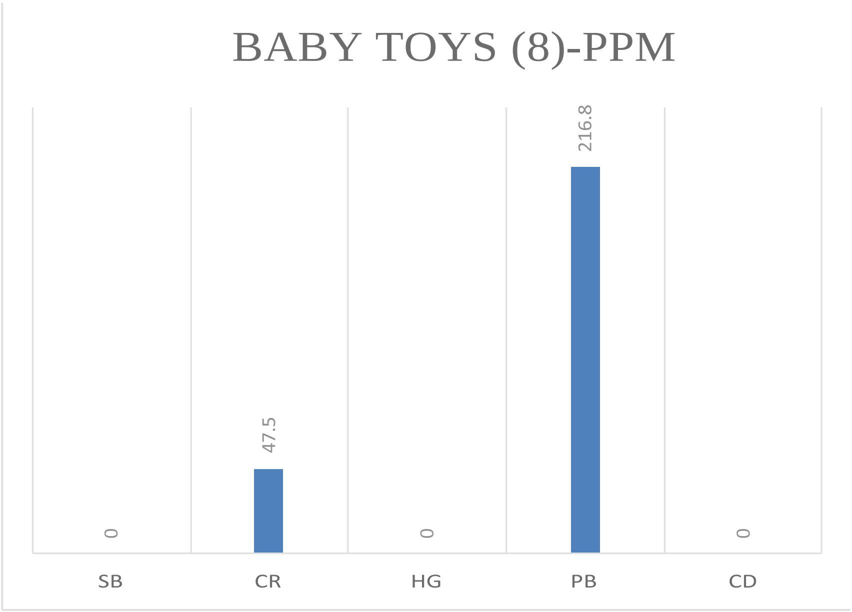

Figure (4.2.1) Baby Toys Number eight concentrations per PPM versus elements contained

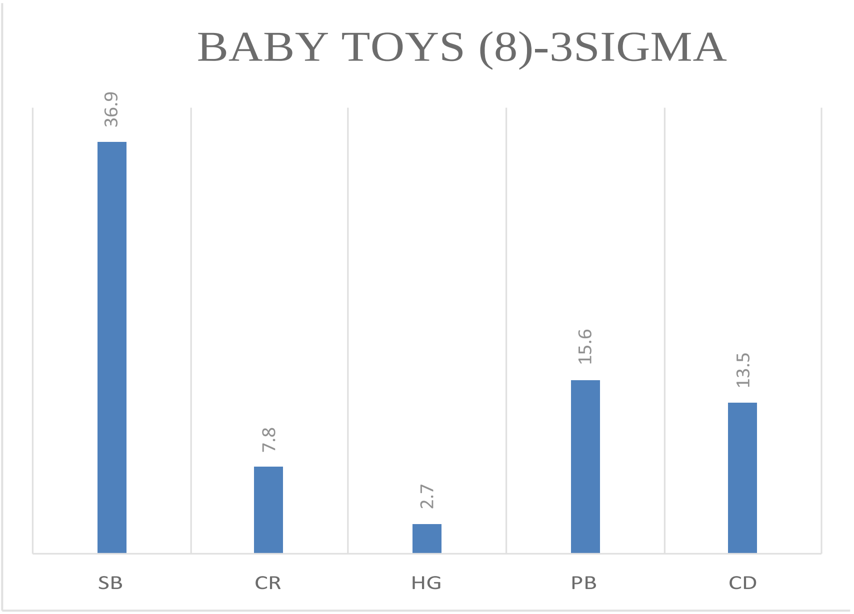

Figure (4.2.2) Baby Toys Number eight concentration per3signma versus elements contained

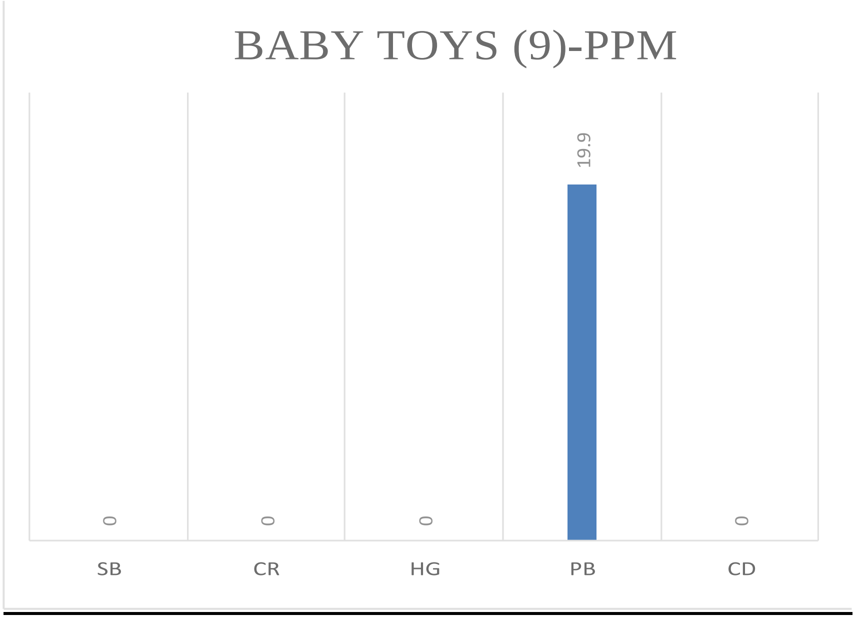

Figure (4.2.3) Baby Toys Number nine concentrations per PPM versus elements contained

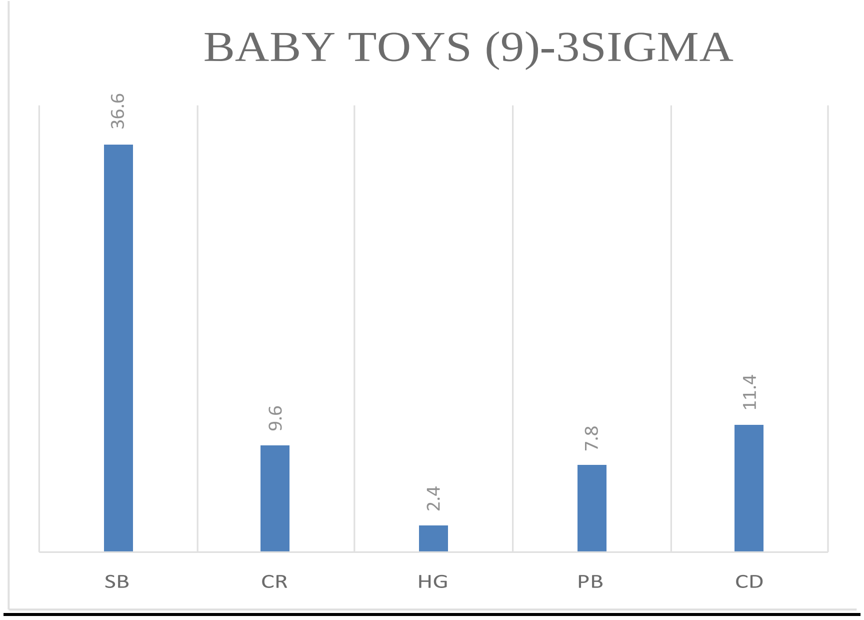

Figure (4.2.4) Baby Toys Number nine concentration per3signma versus elements contained

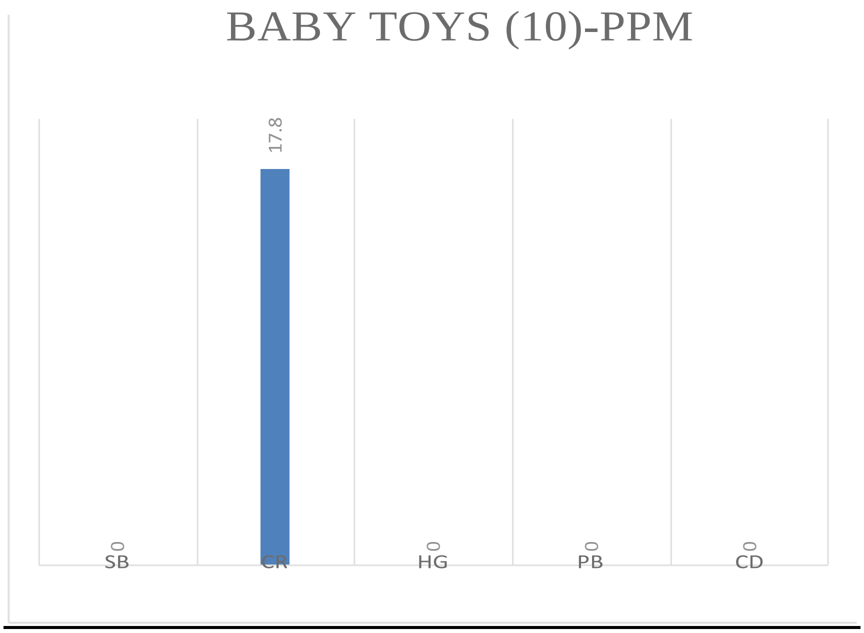

Figure (4.2.5) Baby Toys Number ten concentrations per PPM versus elements contained

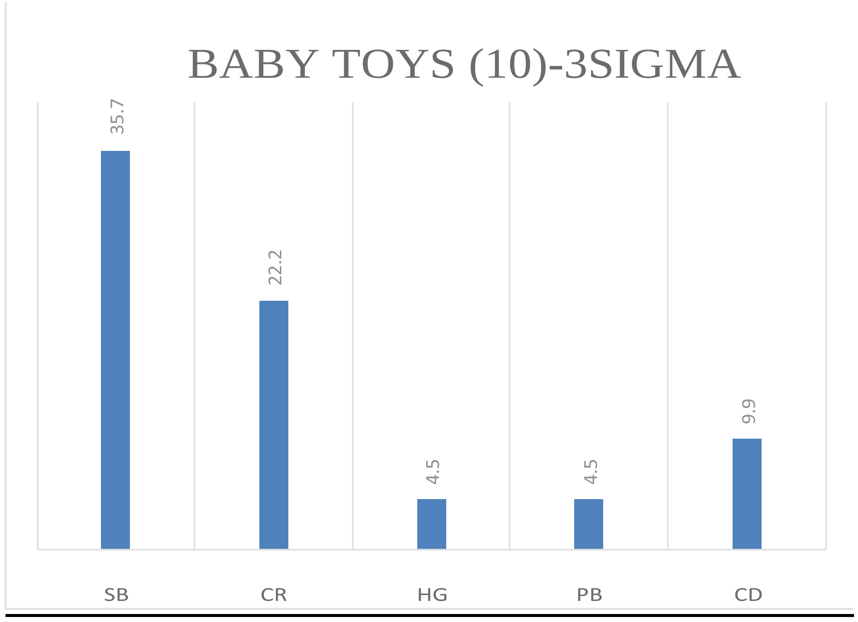

Figure (4.2.6) Baby Toys Number ten concentration per3signma versus elements contained

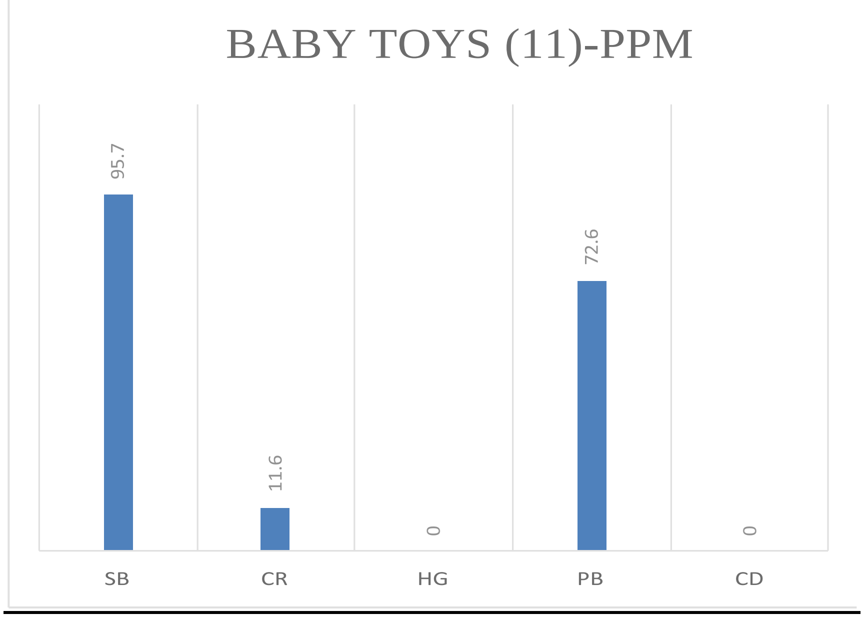

Figure (4.2.7) Baby Toys Number eleven concentrations per PPM versus elements contained

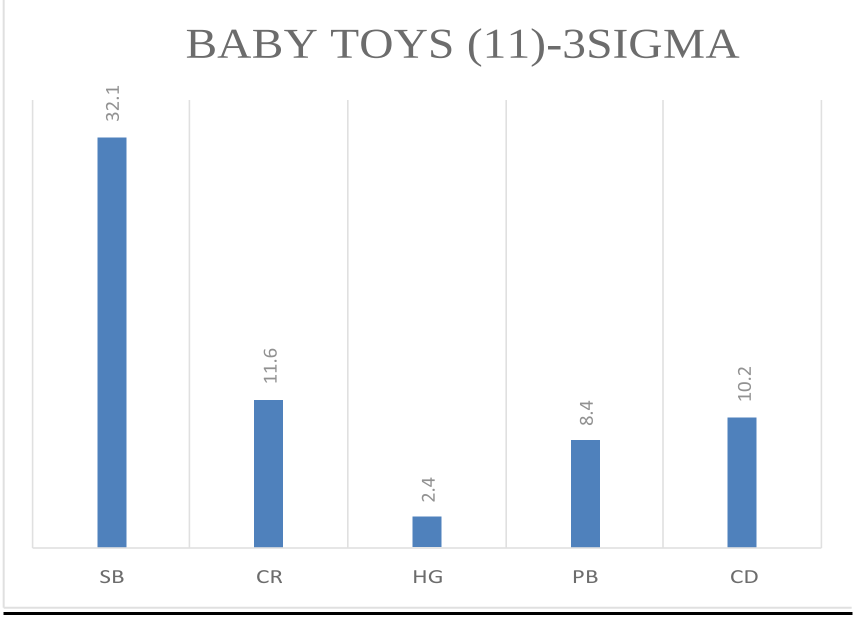

Figure (4.2.8) Baby Toys Number eleven concentration per3signma versus elements contained

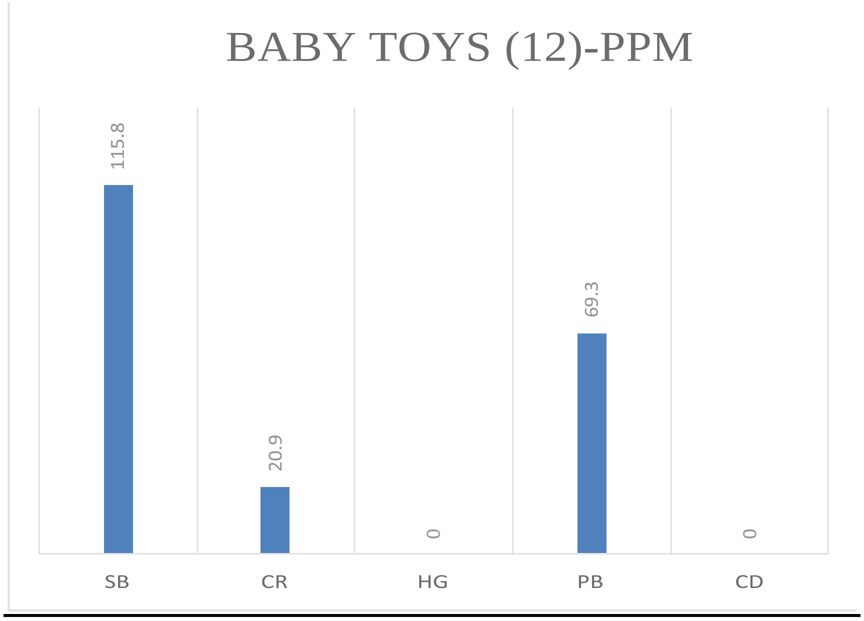

Figure (4.2.9) Baby Toys Number twelve concentrations per PPM versus elements contained

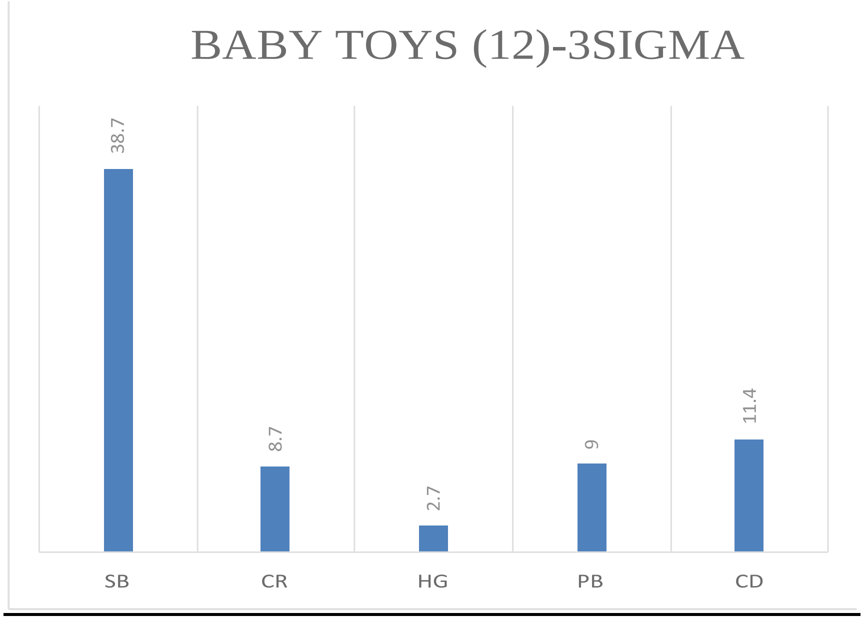

Figure (4.2.10) Baby Toys Number twelve concentration per3signma versus elements contained

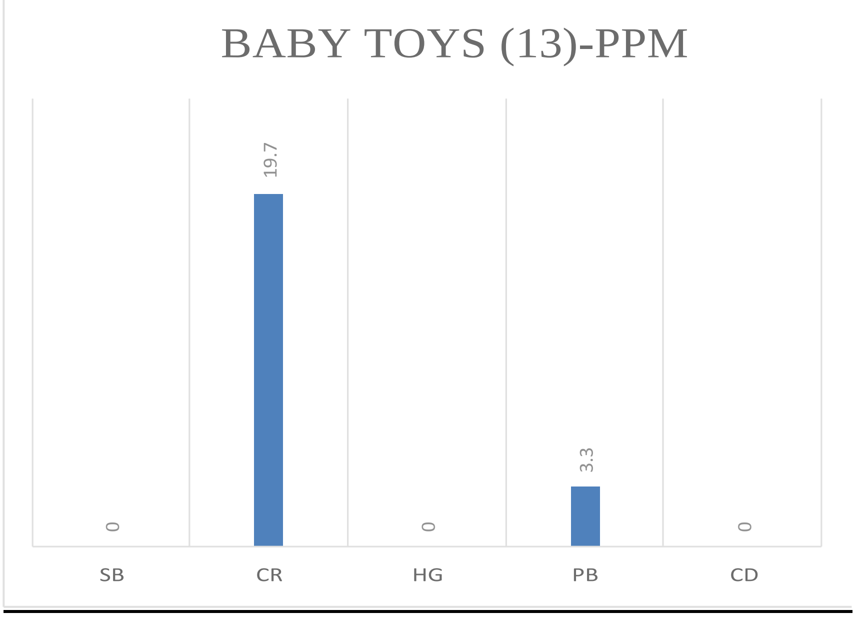

Figure (4.2.11) Baby Toys Number thirteen concentrations per PPM versus elements contained

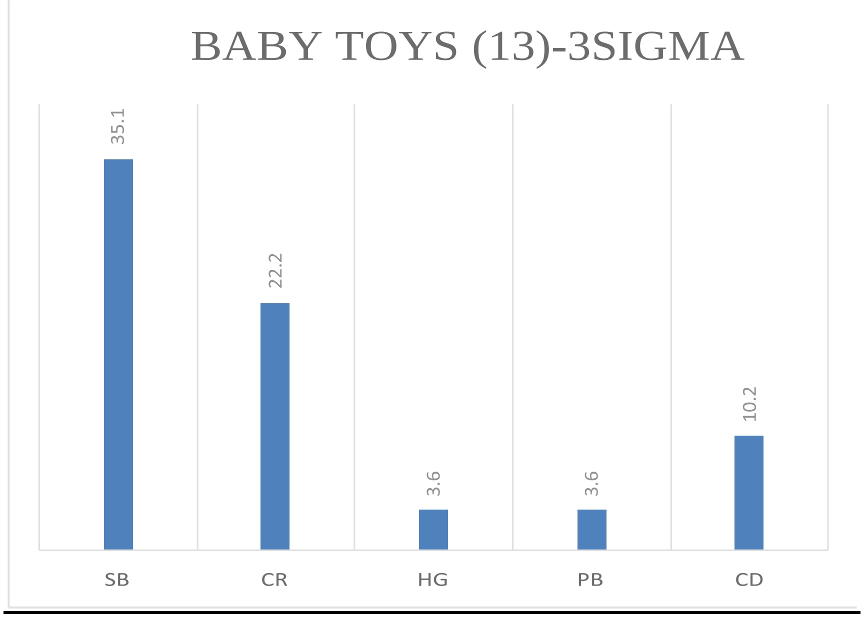

Figure (4.2.12) Baby Toys Number thirteen concentration per3signma versus elements contained

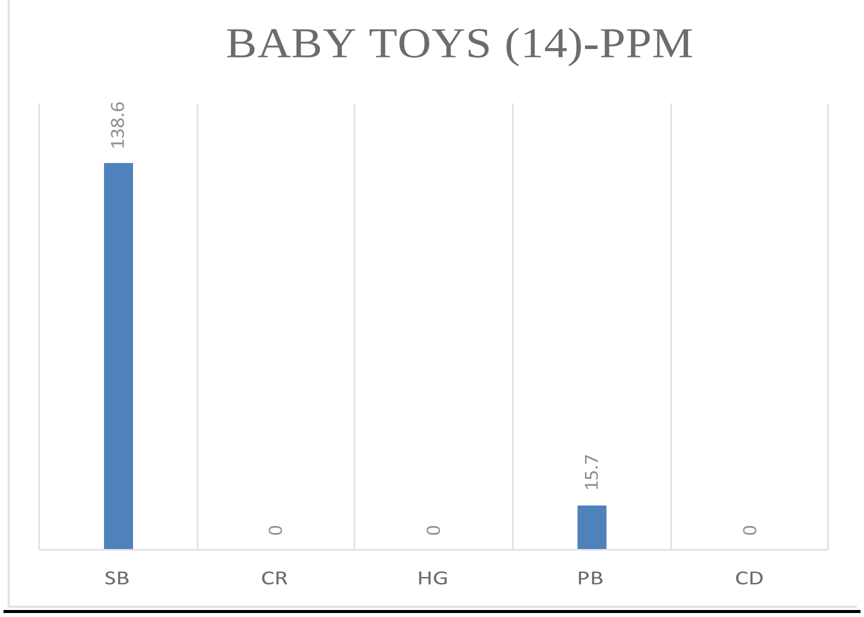

Figure (4.2.13) Baby Toys Number fourteen concentrations per PPM versus elements contained

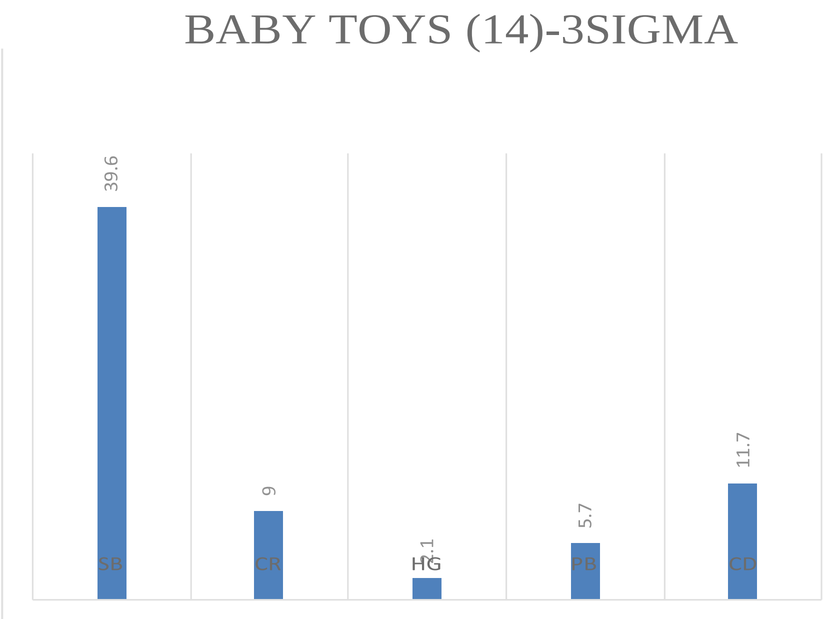

Figure (4.2.14) Baby Toys Number fourteen concentration per3signma versus elements contained

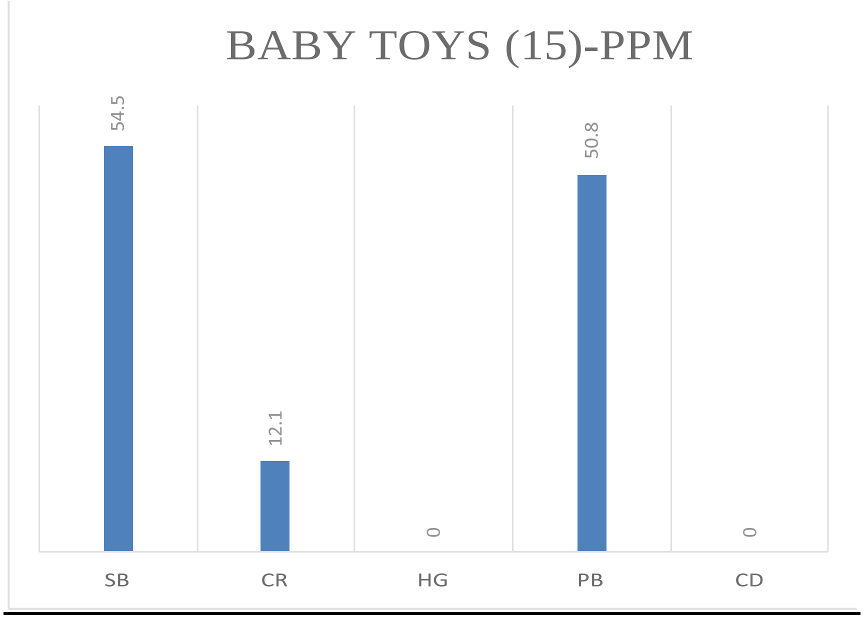

Figure (4.2.15) Baby Toys Number fifteen concentrations per PPM versus elements contained

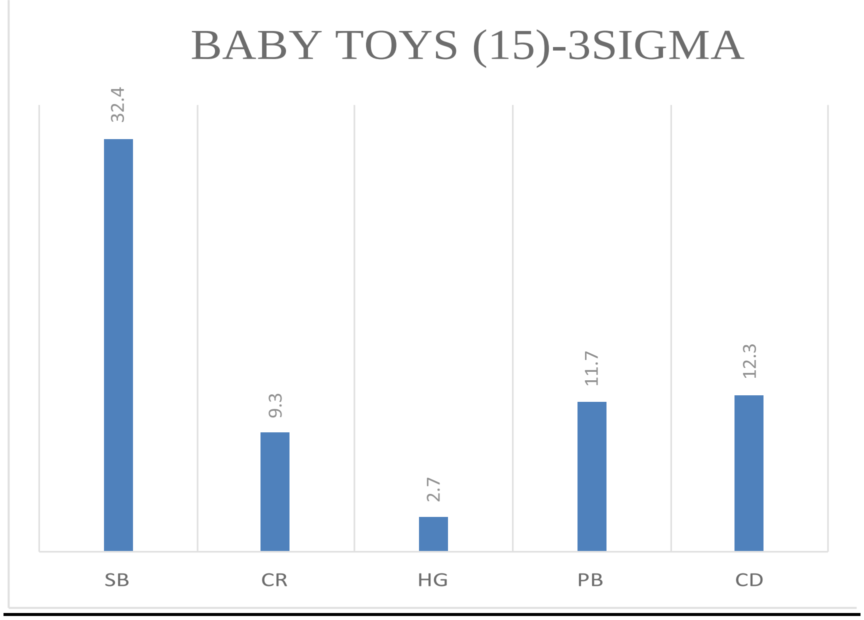

Figure (4.2.16) Baby Toys Number fifteen concentration per3signma versus elements contained

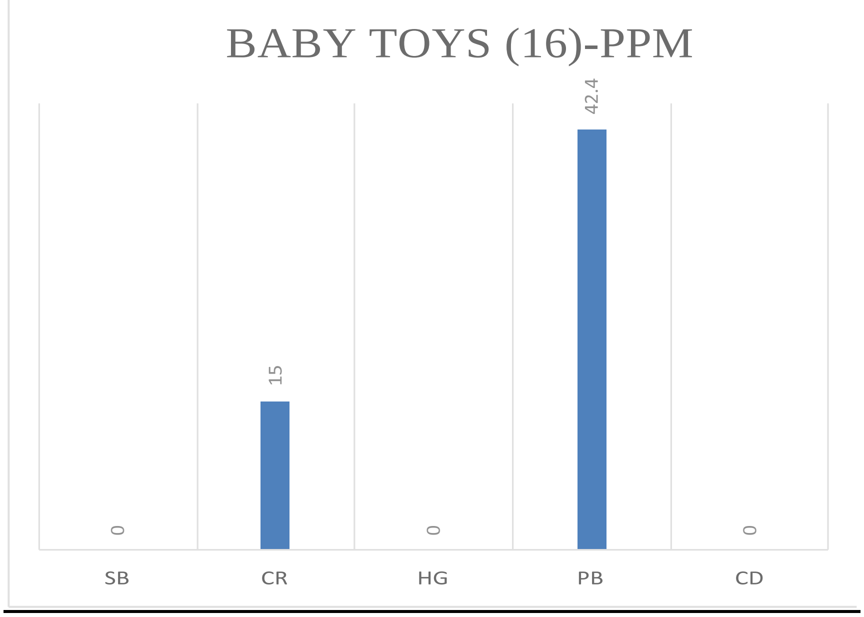

Figure (4.2.17) Baby Toys Number sixteen concentrations per PPM versus elements contained

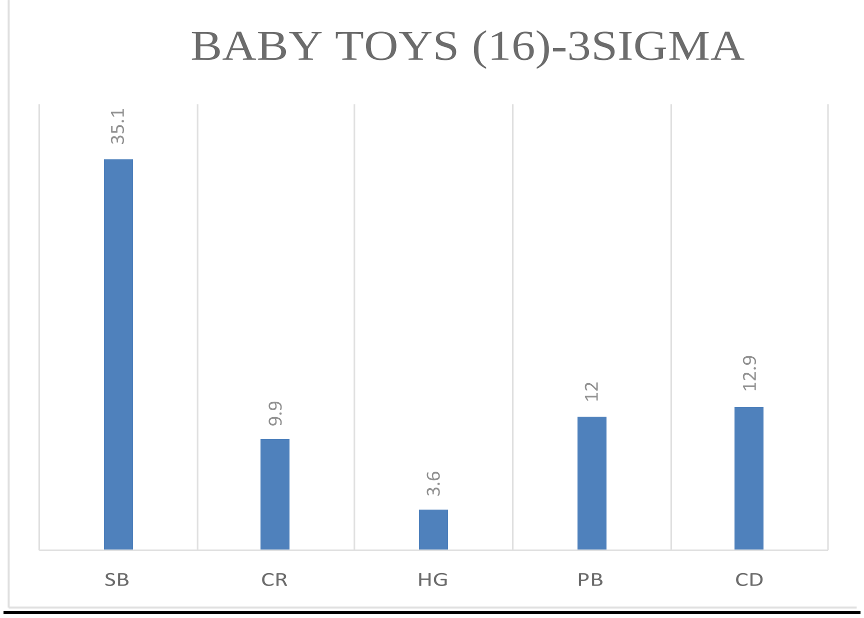

Figure (4.2.18) Baby Toys Number sixteen concentration per3signma versus elements contained

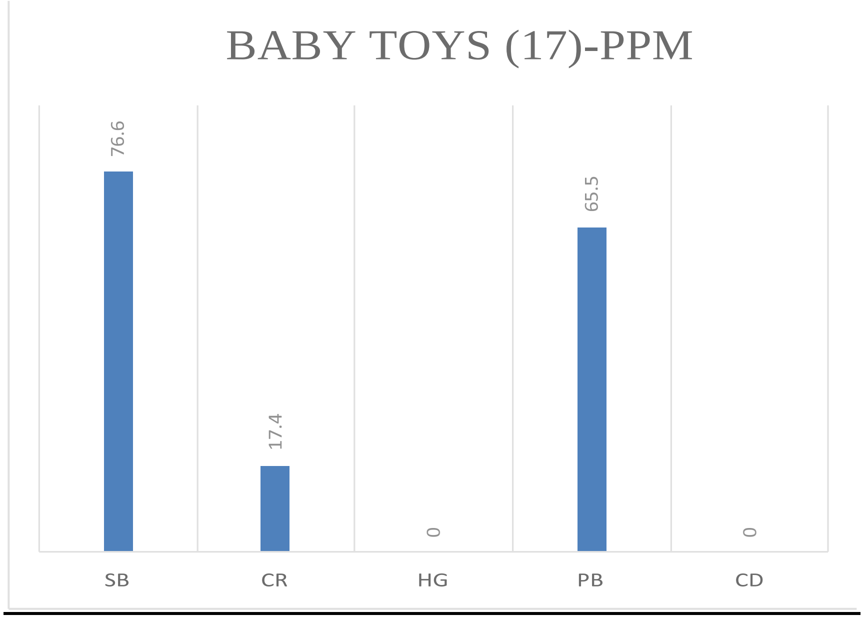

Figure (4.2.19) Baby Toys Number seventeen concentrations per PPM versus elements contained

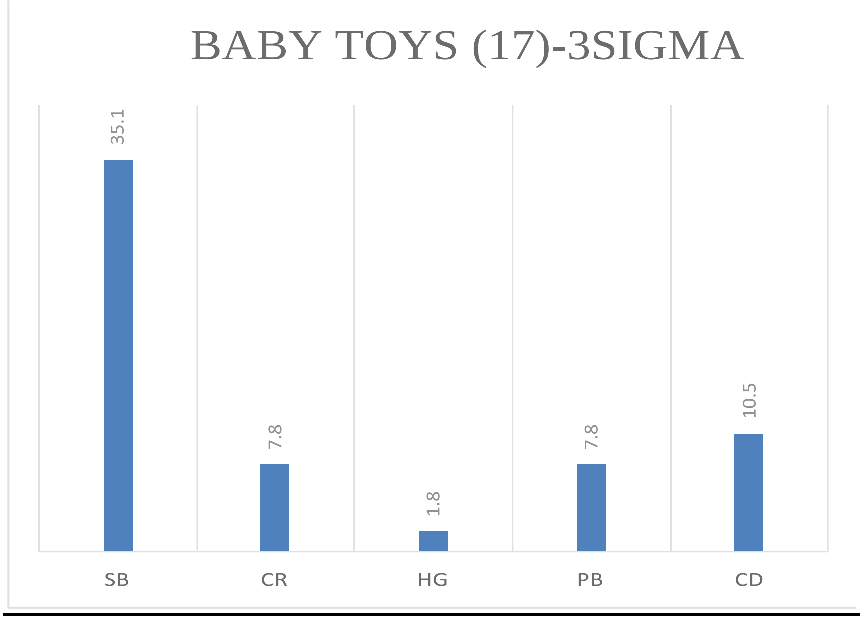

Figure (4.2.20) Baby Toys Number seventeen concentration per3signma versus elements contained

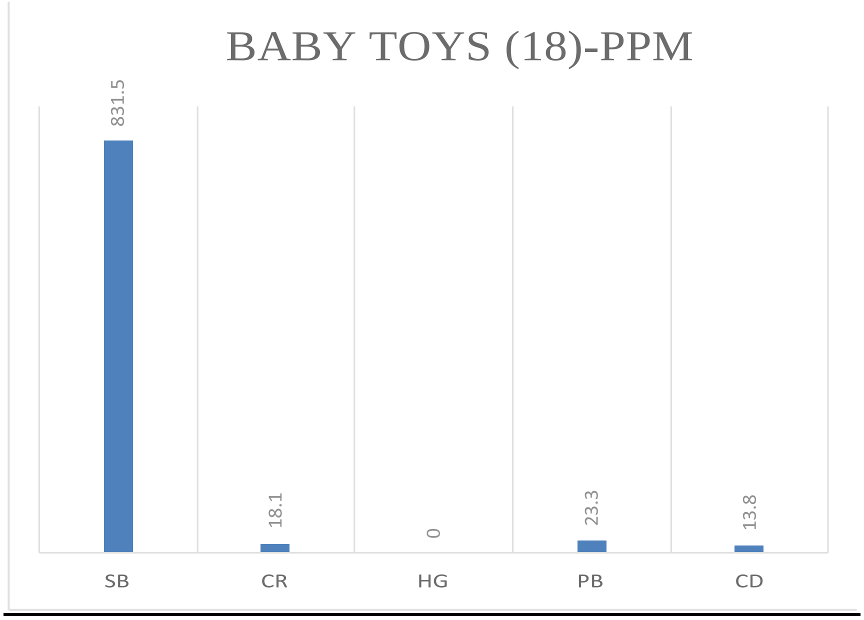

Figure (4.2.21) Baby Toys Number eighteen concentrations per PPM versus elements contained

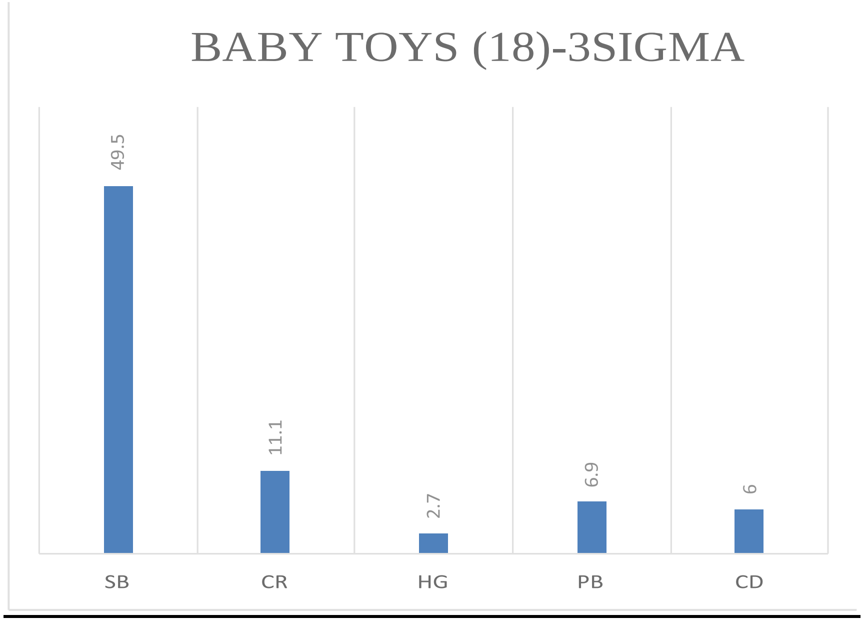

Figure (4.2.22) Baby Toys Number eighteen concentration per3signma versus elements contained

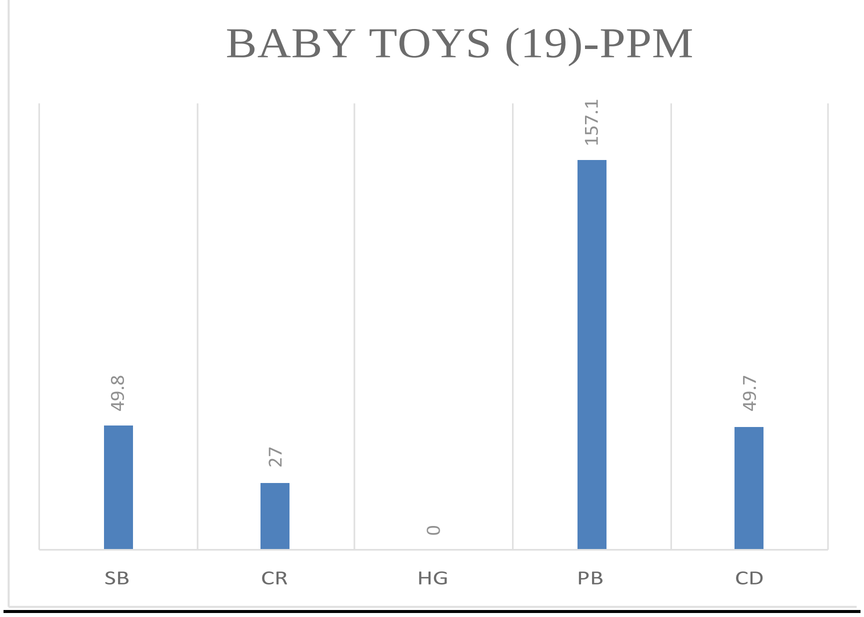

Figure (4.2.23) Baby Toys Number nineteen concentrations per PPM versus elements contained

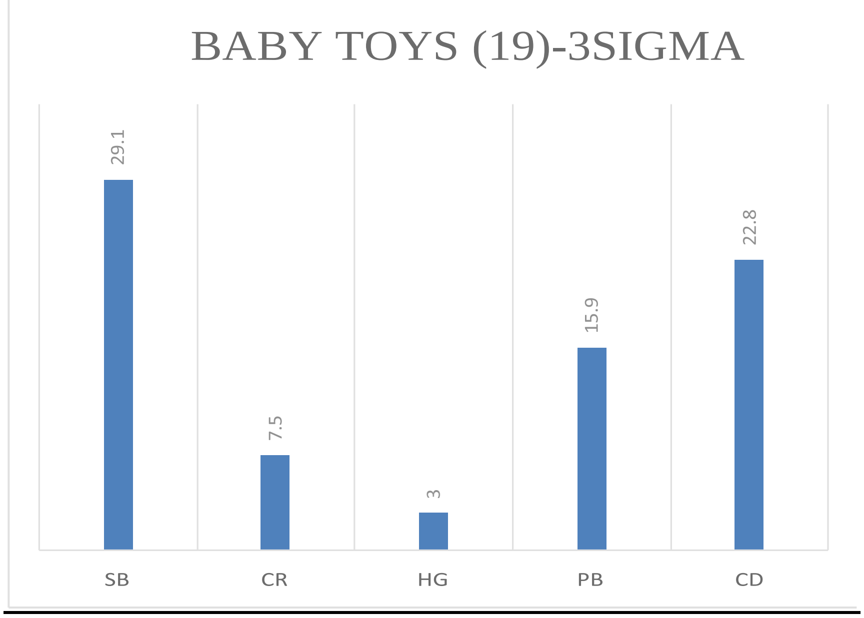

Figure (4.2.24) Baby Toys Number nineteen concentration per3signma versus elements contained

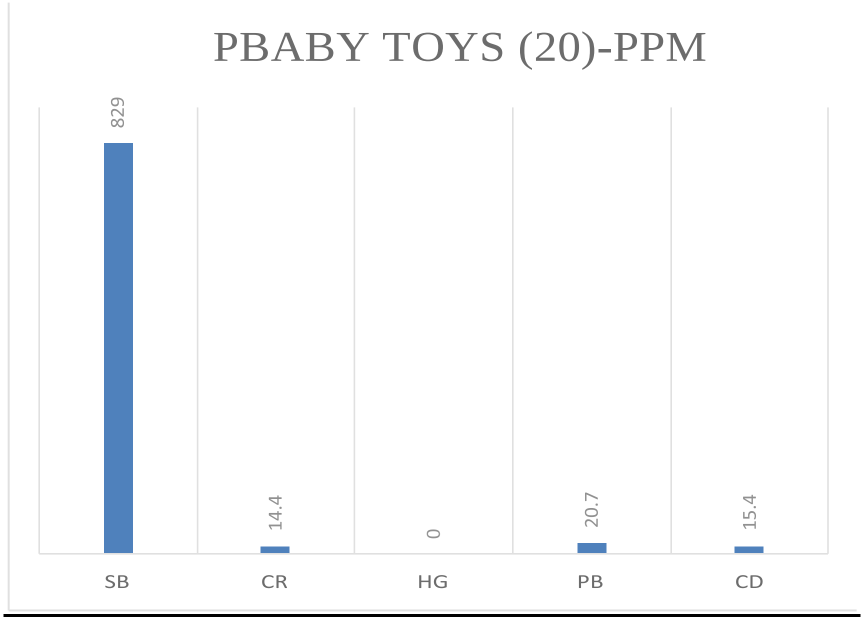

Figure (4.2.25) Baby Toys Number twenty concentrations per PPM versus elements contained

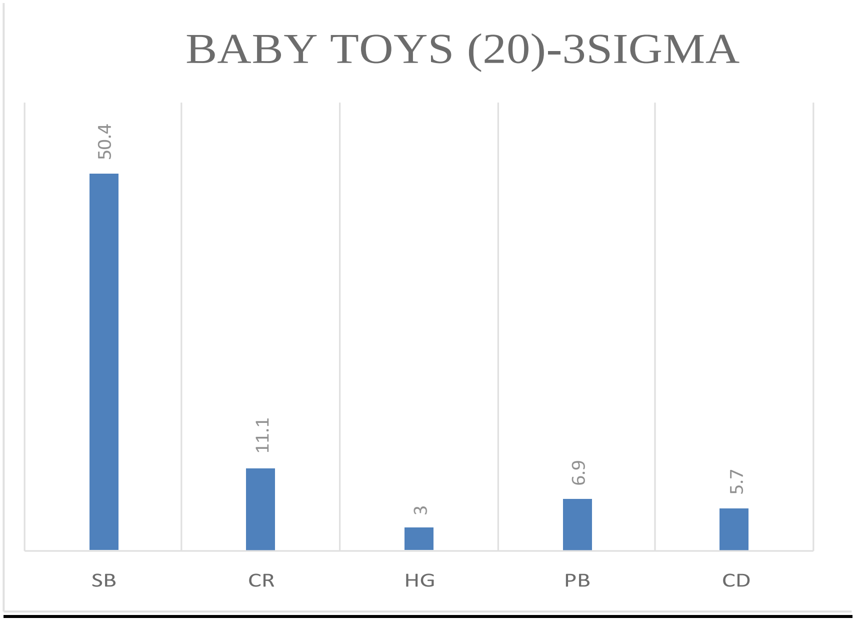

Figure (4.2.26) Baby Toys Number twenty concentration per3signma versus elements contained

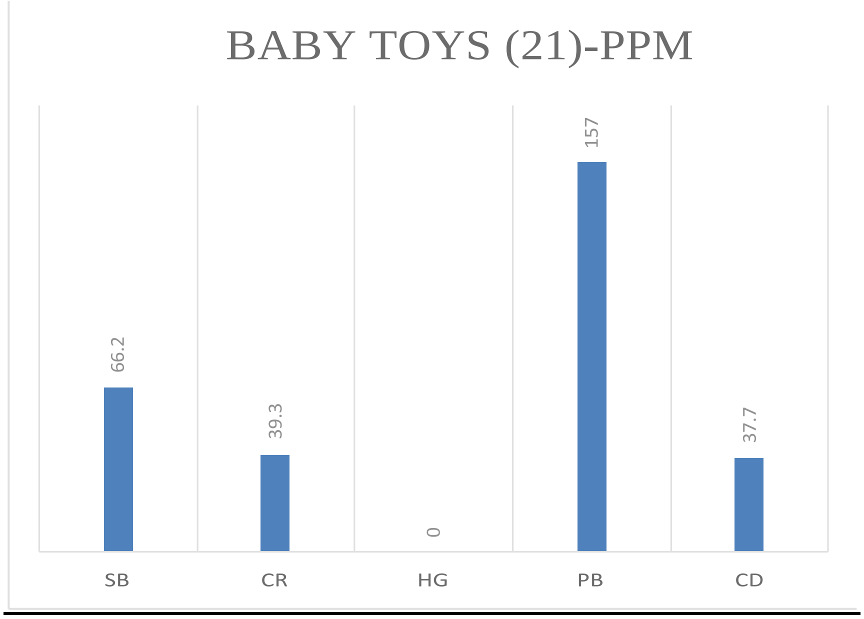

Figure (4.2.27) Baby Toys Number twenty one concentrations per PPM versus elements contained

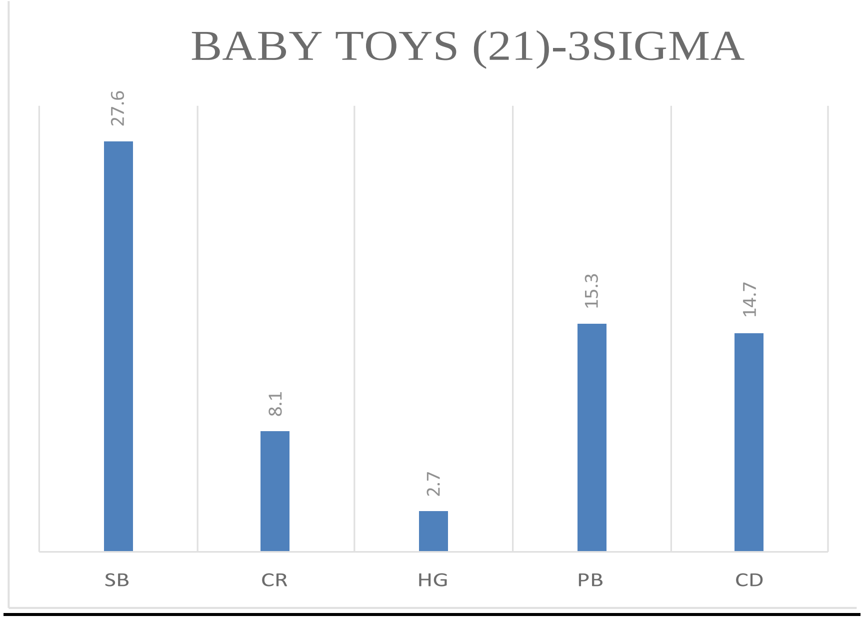

Figure (4.2.28) Baby Toys Number twenty one concentration per3signma versus elements contained

Table (4.3) maximum permissible limit (/ppm) for the elements

elements	Maximum permissible limit /ppm
Pb	90
Cr	25
Br	250
Cd	50
Hg	25
Sb	60
As	25
Se	500

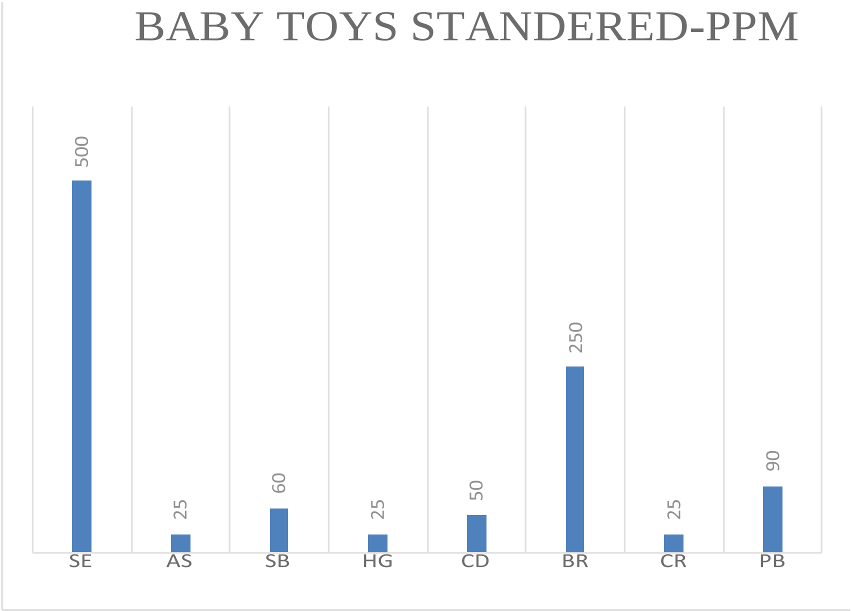

Figure (4.3) Baby Toys standard - ppm

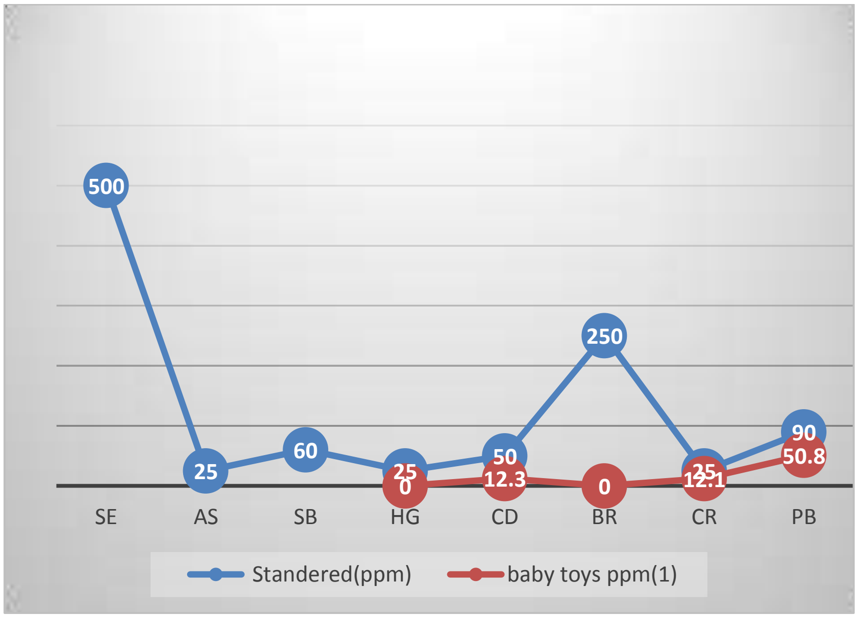

Figure (4.4) Baby Toys Number one concentration ppm with Baby Toys standard - ppm

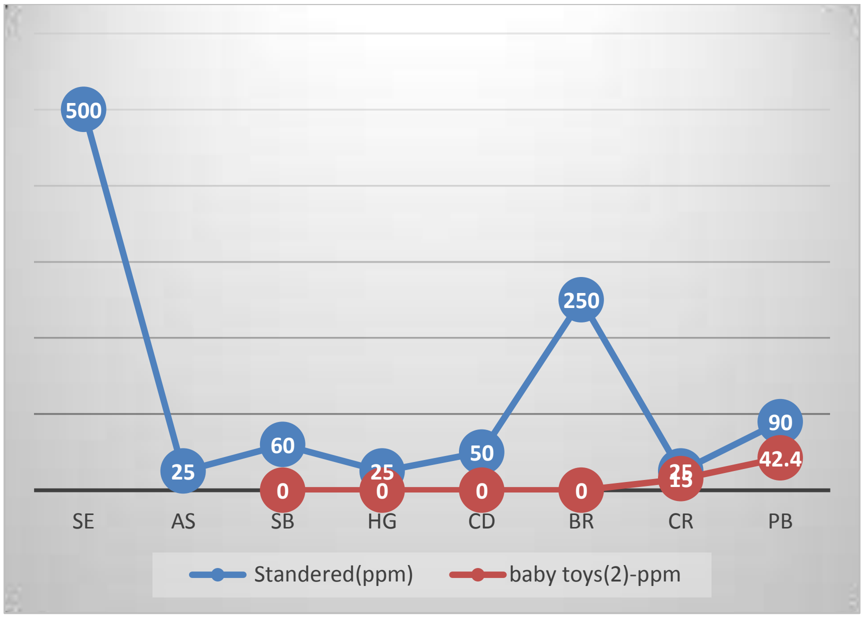

Figure (4.5) Baby Toys Number two concentration ppm with Baby Toys standard - ppm

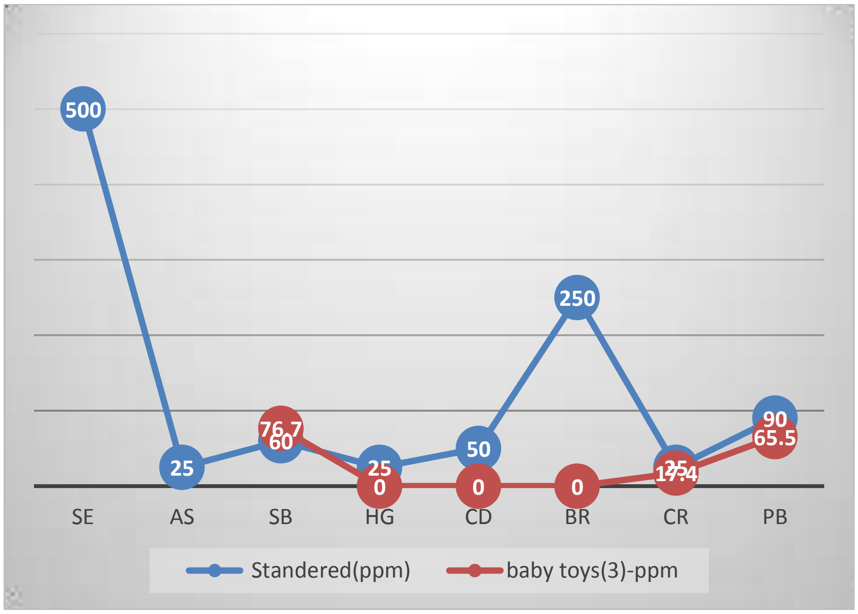

Figure (4.6) Baby Toys Number three concentration ppm with Baby Toys standard - ppm

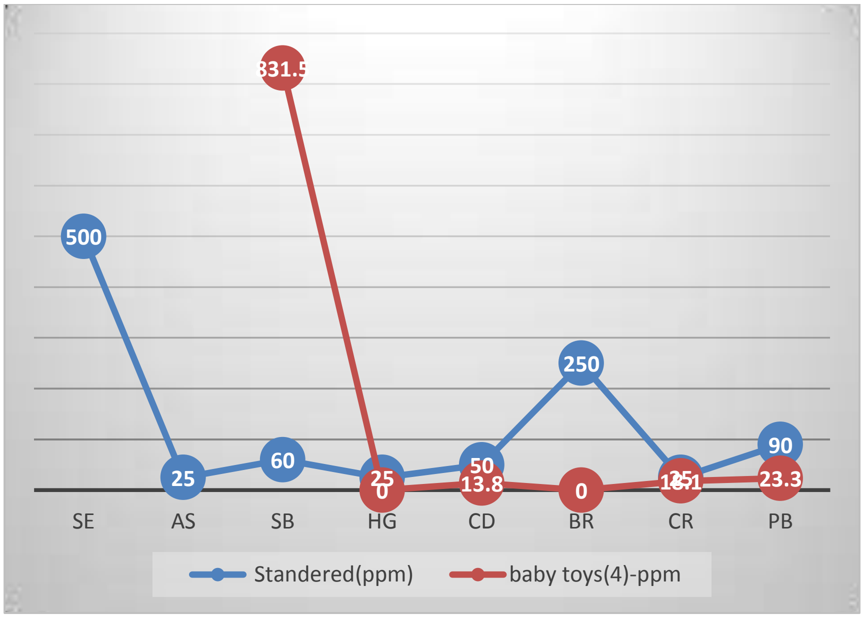

Figure (4.7) Baby Toys Number four concentration ppm with Baby Toys standard - ppm

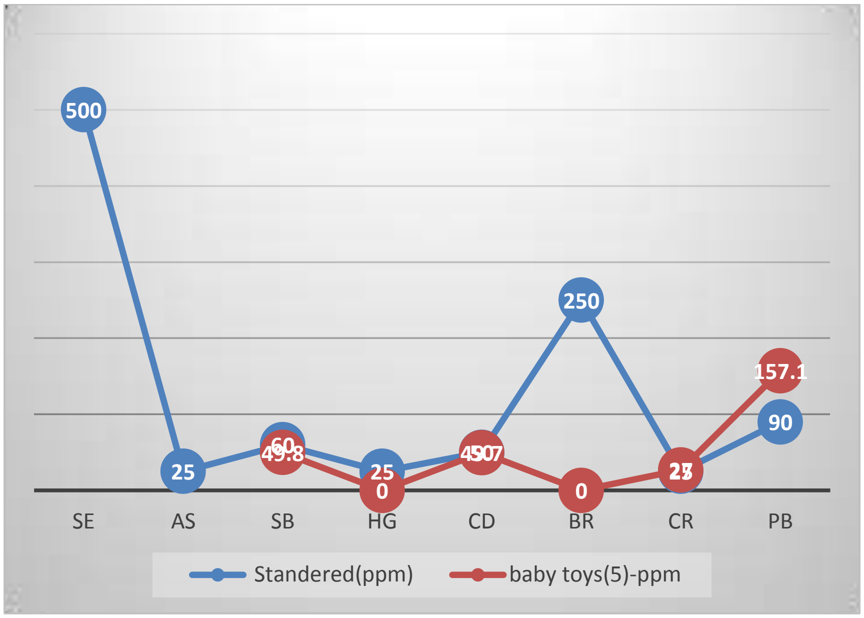

Figure (4.8) Baby Toys Number five concentration ppm with Baby Toys standard – ppm

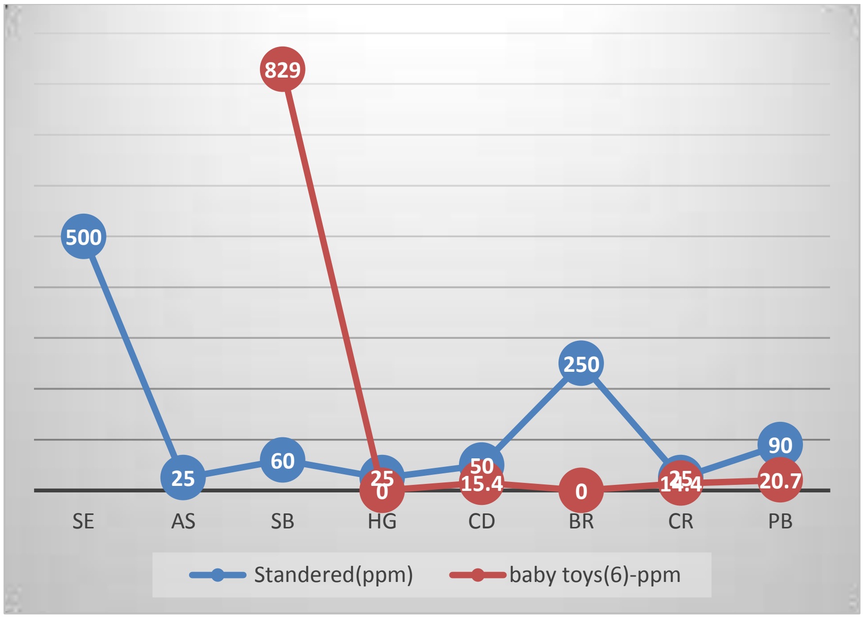

Figure (4.9) Baby Toys Number six concentration ppm with Baby Toys standard - ppm

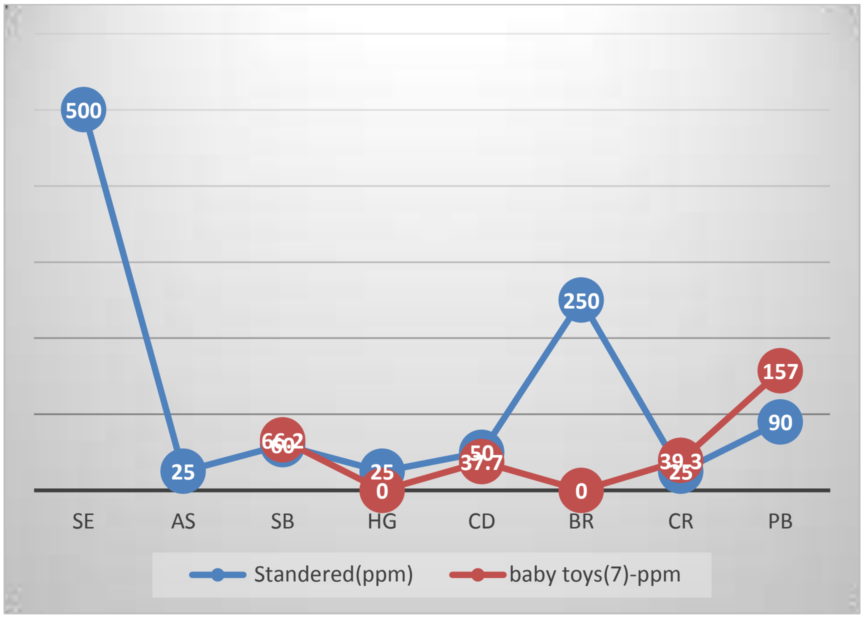

Figure (4.10) Baby Toys Number seven concentration ppm with Baby Toys standard - ppm

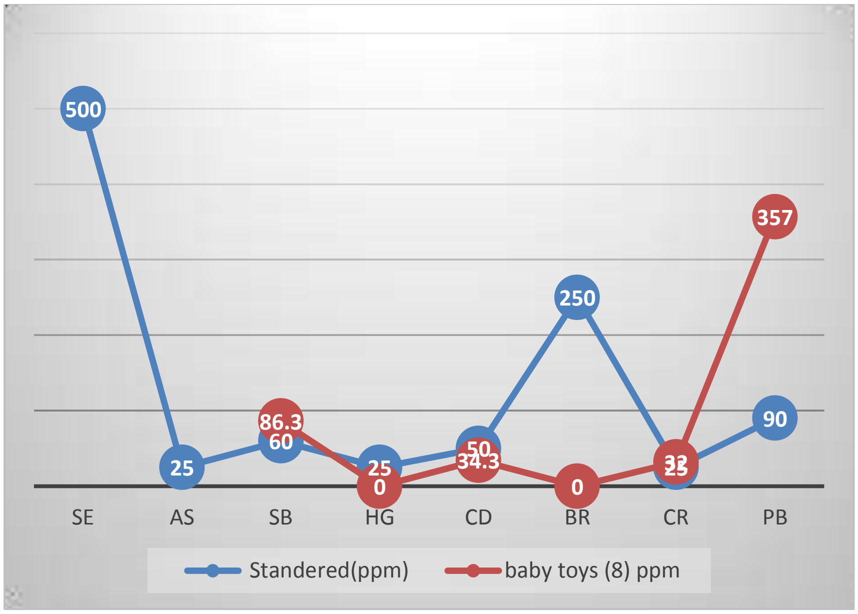

Figure (4.11) Baby Toys Number eight concentration ppm with Baby Toys standard - ppm

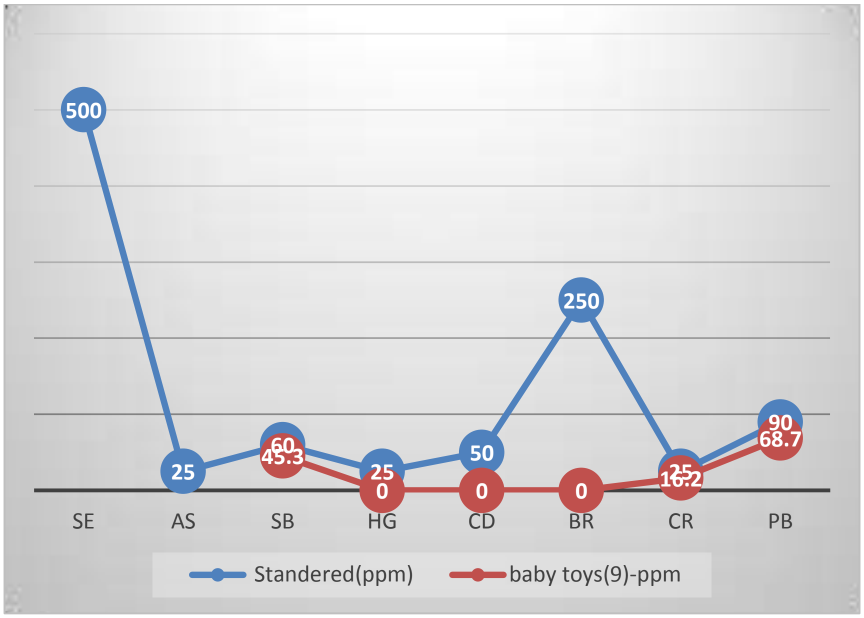

Figure (4.12) Baby Toys Number nine concentration ppm with Baby Toys standard - ppm

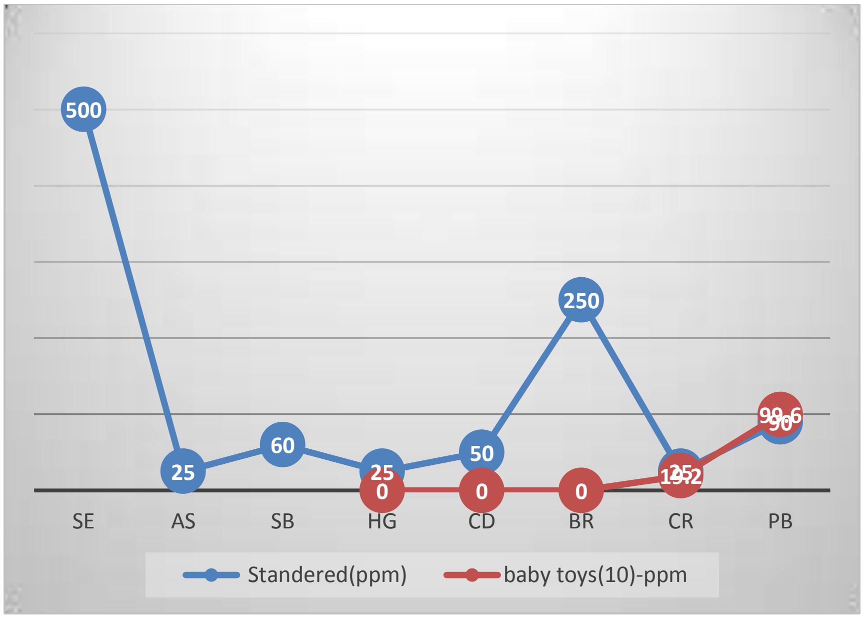

Figure (4.13) Baby Toys Number ten concentration ppm with Baby Toys standard - ppm

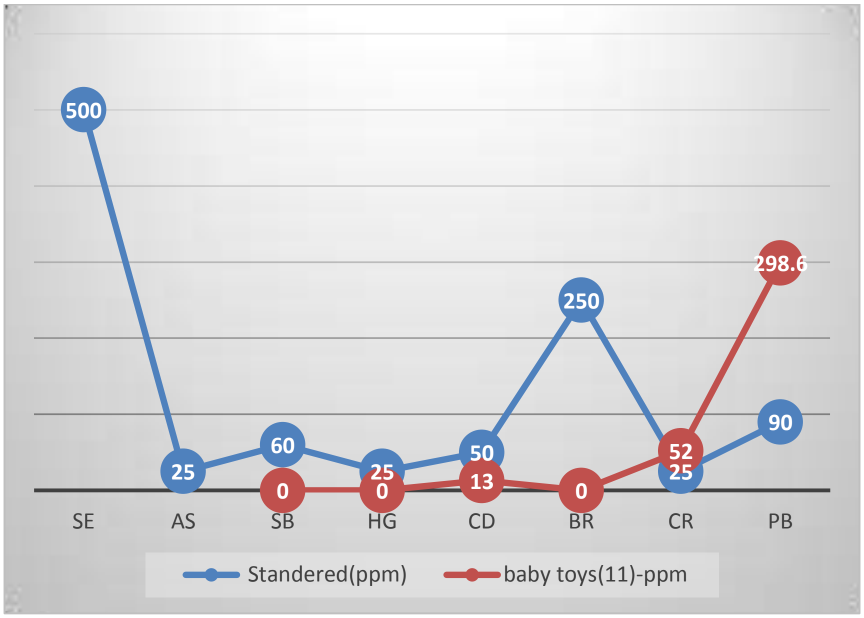

Figure (4.14) Baby Toys Number eleven concentration ppm with Baby Toys standard – ppm

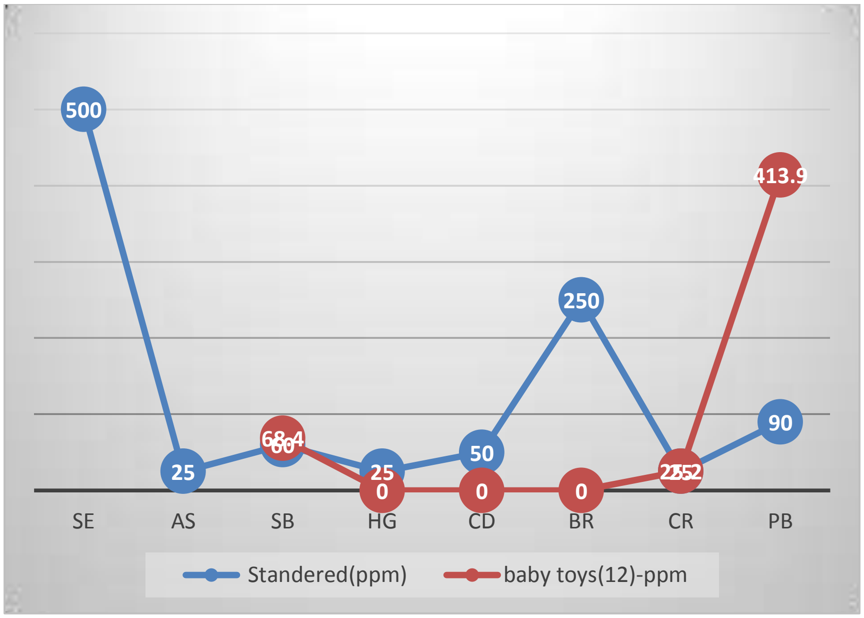

Figure (4.15) Baby Toys Number twelve concentration ppm with Baby Toys standard - ppm

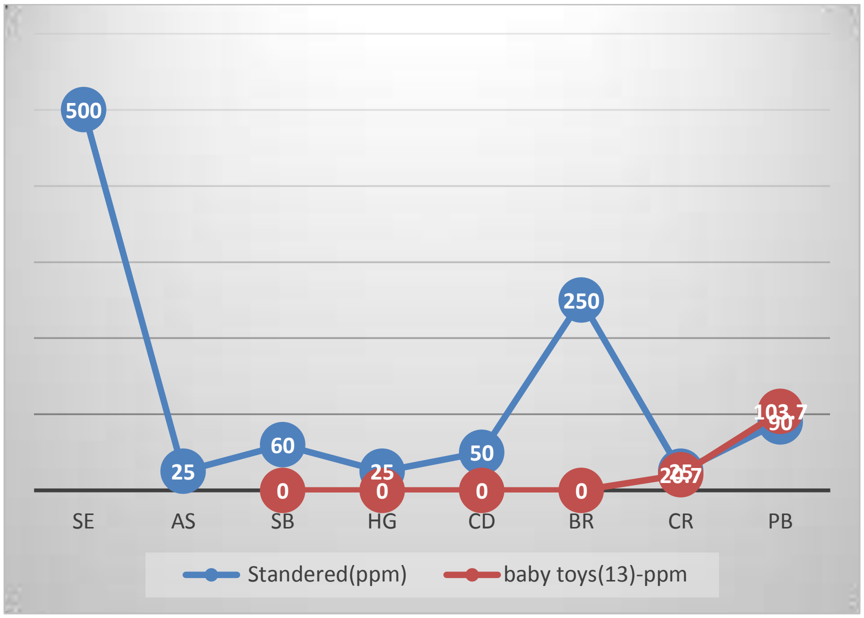

Figure (4.16) Baby Toys Number thirteen concentration ppm with Baby Toys standard - ppm

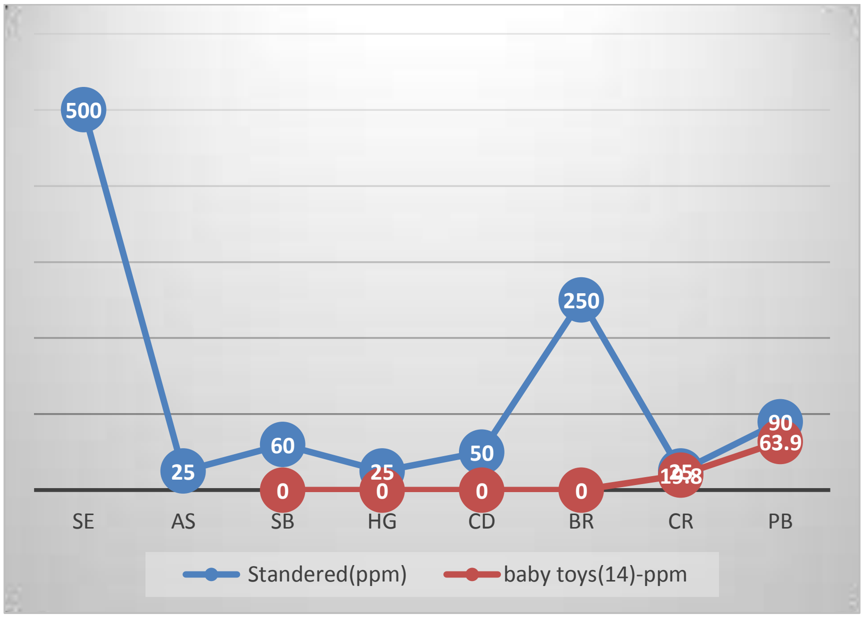

Figure (4. 17) Baby Toys Number fourteen concentration ppm with Baby Toys standard - ppm

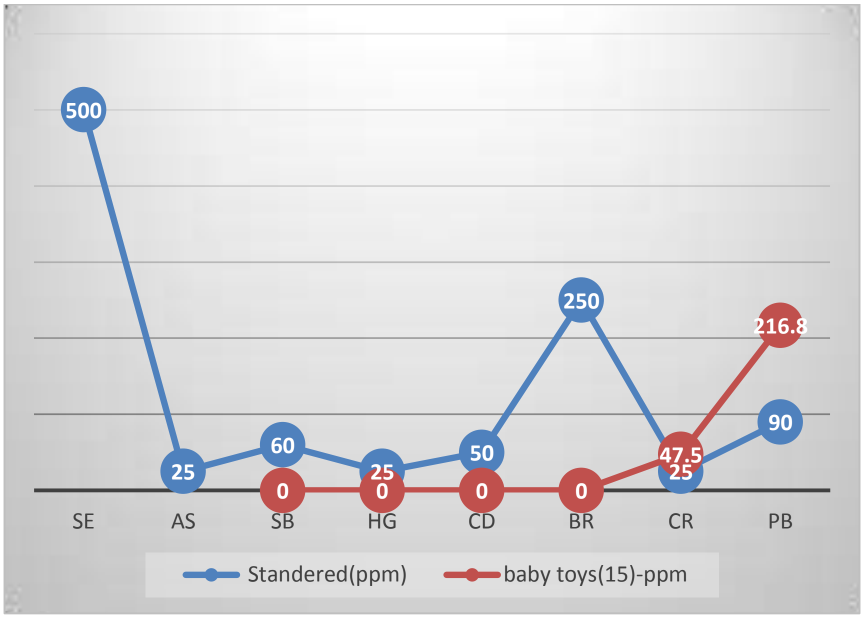

Figure (4.18) Baby Toys Number fifteen concentration ppm with Baby Toys standard - ppm

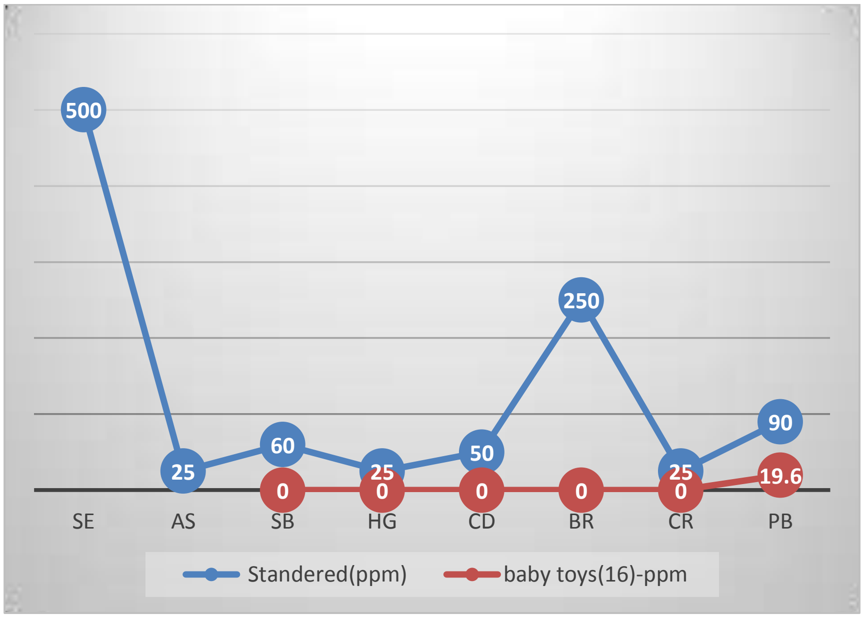

Figure (4.19) Baby Toys Number sixteen concentration ppm with Baby Toys standard - ppm

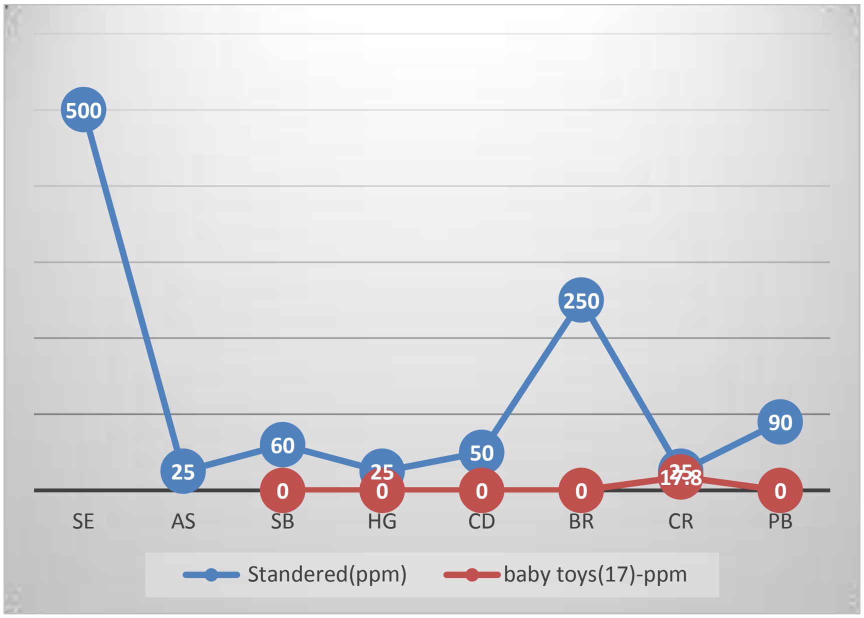

Figure (4.20) Baby Toys Number seventeen concentration ppm with Baby Toys standard – ppm

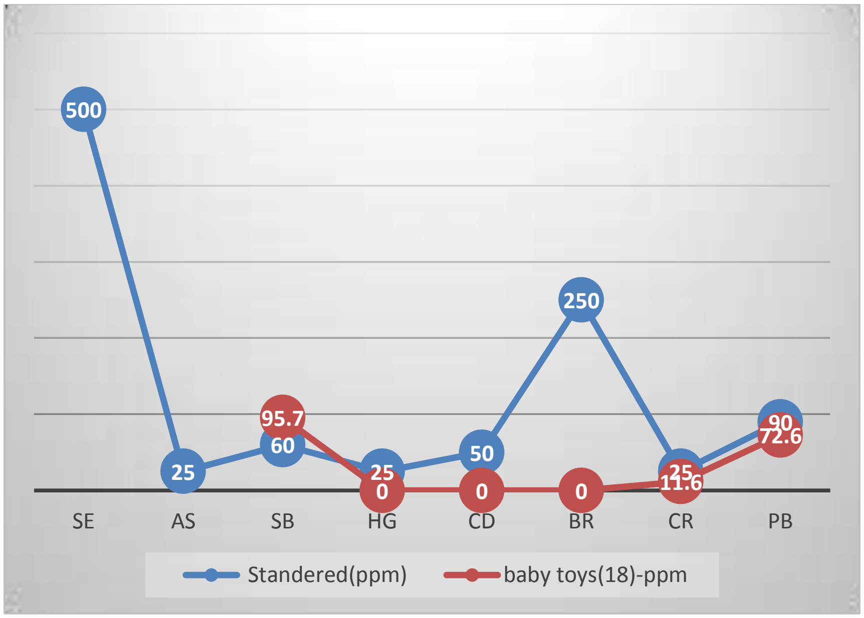

Figure (4.21) Baby Toys Number eighteen concentration ppm with Baby Toys standard - ppm

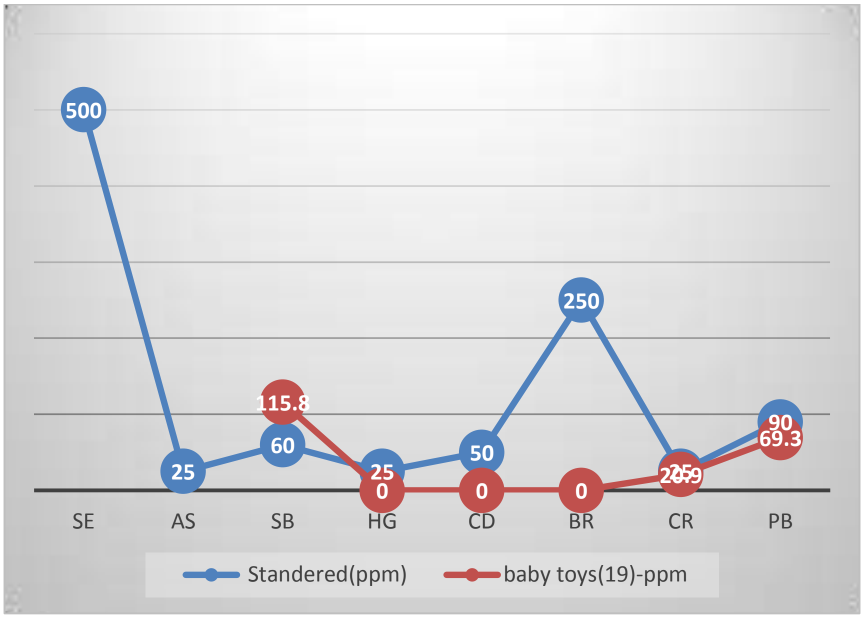

Figure (4.22) Baby Toys Number nineteen concentration ppm with Baby Toys standard – ppm

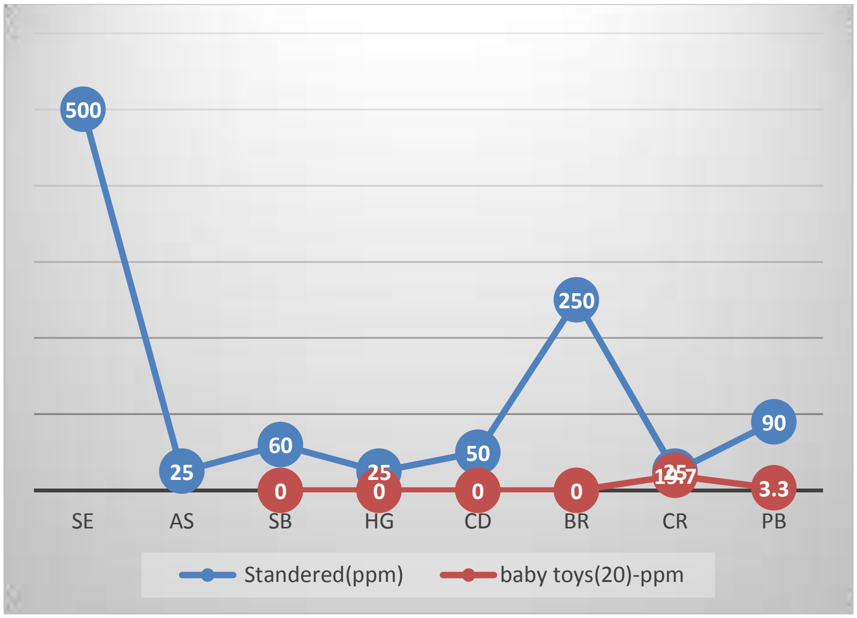

Figure (4.23) Baby Toys Number twenty concentration ppm with Baby Toys standard - ppm

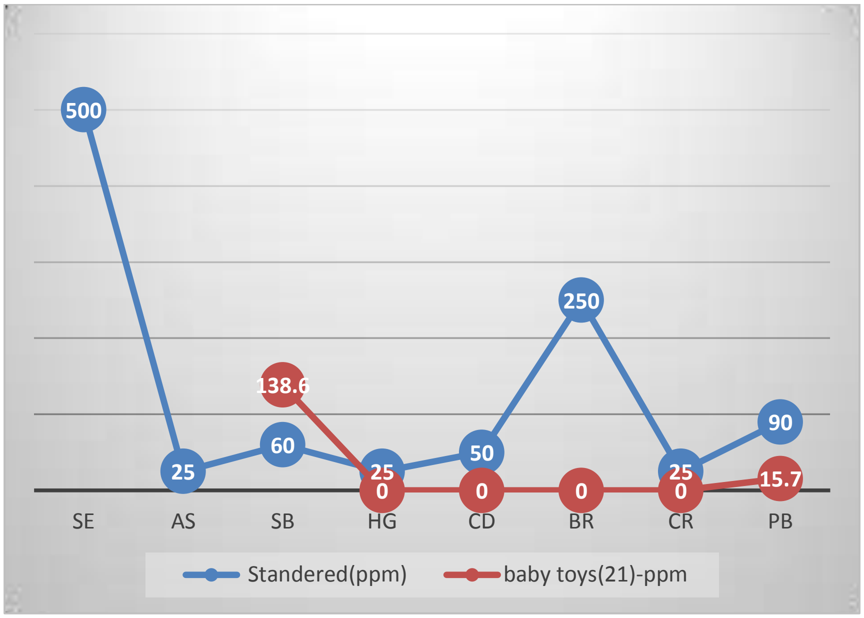

Figure (4.24) Baby Toys Number twenty one concentration ppm with Baby Toys standard - ppm

4.5 Discussion

Table (4.1) shows the concentration of elements (ppm and 3sigma) exist in different toys made in china which graphed in figures (4.1.1 up to 4.1.14)

Table (4.2) shows the concentration of elements (ppm and 3sigma) exist in different toys made in Taiwan which graphed in figures (4.2.1 up to 4.2.28)

Table (4.3) the concentration of elements (ppm and 3sigma) exist in different toys made as standard which graphed in figures (4.3)

All except two of the toys products tested contained detectable levels of Pb and Sb higher than standard value of concentration. Far the most common elements detected were Sb and Pb .

used in products either specifically marketed for children toys, or for use in applications which could entail children experiencing significant exposure 73 through regular or prolonged contact. In some cases, chemicals with known significant hazards are being used. Despite being subject to widespread and progressive regulation leading to phase-outs in other applications, they are not currently regulated in relation to their use as PVC additives.

Many of the regulations being proposed to deal with the hazards of the additives in PVC is based on trying to calculate the degree of exposure that is "safe" for children.

4.6 Conclusion

Despite the various regulatory initiatives which have been, or are currently being developed in relation to PVC additives, these chemicals are still being widely

4.7 Recommendation

1. Avoid plastics with recycling material.
2. Purchase baby bottles with glass options.
3. Never heat or microwave food or drink in any plastic containers, as leaching of toxic chemicals from plastic to food or liquid may occur. Use a paper towel instead of plastic wrap to cover food in the microwave.
4. Use PVC-free plastic wrap (buy plastic wrap and bags made with polyethylene).
5. Minimize the use of canned foods and canned drinks as many are lined with BPA.
6. Choose phthalate-free toys. Look for toys labeled "phthalate-free" or "PVC-free". Choose toys made from polypropylene or polyethylene.
7. Purchase phthalate-free beauty products.
8. Discard all plastic food containers with scratches, especially baby bottles, Sippy cups and infant feeding plates and cups.

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