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Determination of some trace elements in white oil based paints and pigments

Thesis M.Sc.

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وَمَا أُوتِيتُمْ مِنَ الْعِلْمِ إِلَّا قَلِيلًا
and of knowledge ye have been vouchsafed but little.

Dedication

To the spirit of my father
and
to my dear mother

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Abbreviations:

ASTM	American Society for Testing and Materials
AAS	Atomic Absorption Spectrometry
B.C.	Before Christ
BSI	British Standard International
CPSC	Canadian Paint and Coating Association
CPSIA	Consumer Product Safety Improvement Act
EPA	Environmental Protection Agency
GFAAS	Graphite Furnace Atomic Absorption Spectrometry
HCL	Hollow –Cathode Lamps
HUD	Housing and Urban Development
ISO	International Organization for Standardization
kV	Kilovolt
R^2	Linearity
μA	microampere
OSHA	Occupational Safety and Health Administration
ppb	part per billion
ppm	part per milliom
PEL	Permissible Exposure limit
PVC	Polyvinyl chloride
±SD	Standard Deviation
±SEM	Standard Error Mean
TLV	Time limit value
TWA	Time Weighted Average
UV-radiation	Ultra Violet radiation
XRF	X-Ray Fluorescence

ABSTRACT

Industrial development in the last few decades has led to a range of environmental problems. In this study, levels of some trace metals (Cd, Cr, Pb,) have been measured in the white oil paint samples of five different Libyan paint companies in Benghazi city using the energy dispersion x-ray fluorescence spectrometer (EDXRF) and the color pigment ingredient samples (blue, green, red and yellow) collected of foreign companies using furnace graphite atomic absorption spectrometry.

We found different concentrations of the three elements (Pb, Cd and Cr) in 30 samples of white oil paints samples among the five companies. These variations were found through paint cans' serial numbers as well as their batch numbers.

The results of this study showed that the concentration of trace elements in 36 samples of oil based paint showed that the average concentration of lead between (292 - 998 mg/Kg), cadmium between(3-38 mg/Kg) and chromium between (0 - 61 mg/Kg). Also, have different lead concentration in two serial numbers, Comparison of our results obtained were higher than Chinese Standards (Pb 90 ppm), but they were compatible with Libyan Standard Specifications (600 ppm). For cadmium the results were less than Chinese Standards (Cd $\leq$ 75 ppm) and for chromium were also less than Chinese Standards (Cr $\leq$ 60 ppm).

For pigments, we found that the concentration of the three elements in all pigments were less than the allowed limit of Standard Specifications.

As a result, we recommend performing quality control tests on all paints and their products before they reach the consumers as their importance in their daily lives, and to be sure all products are compatible with the Standard Specifications.

Chapter 1

Introduction

1.1. Paints

Today, paints are used almost everywhere in our daily life such as on buildings, furniture, cabinets, refrigerators, wires of electrical motors, cassettes and videotapes, compact discs, inside and outside of cans, ships, aircrafts, steel bridges, storage tanks and cars. They are used for decoration purposes as well as for protecting surfaces against various environmental effects like UV-radiation, chemical invasion and mechanical stresses (Wicks *et al.,* 2007).

Paint is the general term for many products utilized for different purposes. The major use of paints is to cover the outside surface of different buildings and metal surface to prevent weather damage and corrosion. It is also applied to interior residential walls and objects for protection and decoration purposes. Metal and metal oxides have long been added to paints for pigmentation, film strength, spreading quality and weather resistance (Turner, 1980).

Two most important components of paints are colouring matter (pigment or dye) and binder (medium). Often different additives are add to paint to enhance some properties of the paint or to make it cheaper There are many different paints by chemical composition of the binder: oil paints, tempera paints, acrylic paints, alkyd paints ,watercolor, etc. To thin the paint to the best consistency for the work, diluent (solvent) must be used. A diluent may be a solvent used to decrease the concentration or viscosity of paint. It can be added to the mixture only to a limited extent without causing precipitation of solid pigment (Gettens and Stout, 1966).

The best known diluents (solvents) are turpentine, mineral spirits (white spirits – hydrocarbon petroleum distillate), different organic solvents (aromatic, esters, ketones, etc.), water (Caddy, 2001 and Seymour, 2003).

Metals are present in the inorganic pigments of paints and play an important role in the ability of the paint to perform its function. Metal content of pigment compounds not only produces colour but also contributes to other chemical and physical properties of paints such as rust inhibitive characteristics and durability. However, inorganic pigments may contain such toxic elements as lead, chromium, cadmium and cobalt (Paudyn and Smith 1993 and Saron and Felisberti, 2006).

Today, the toxicity and contamination potential of heavy metals in paints has prompted great interest in daily life. (Wang *et al.,* 2007).

1.1.1. History of paints

The earliest evidence of well-preserved prehistoric paintings, dating from the 16th millennium B.C. can be found in caves in Southern France, Spain and South Africa (Stoye and Freitag, 1998).

During the period 3000–600 B.C. many paint-making advances were made by the Egyptians. They not only developed pigments with a wider range of colors but are also credited with producing the first synthetic pigment (Egyptian Blue) and developing the first lake pigments. Preservative paints and varnishes were also used during this time (Lambourne and Strivens, 1999).

The first painted objects come from China. Furniture and utensils were covered with a layer of paint in an artistic design. The oldest tradition work dates from around 200 B.C. The lacquer used was the milky juice from the bark of the lacquer tree. This was colored black or red with minerals, and later also with gold dust or gold leaf (Stoye and Freitag, 1998).

In Medieval Europe, the art of paint, as well as the art of manufacturing paint was progressing. There is much literature on the subject of making various types of coatings and the ingredients used, but it is difficult for the uninitiated to determine just what is meant by certain raw materials whose names are to a great extent unknown today. However, it is known that the advent of oil as an ingredient in manufacturing varnish occurred sometime around the sixth century. Still the preferred medium for manufacturing paint was egg albumin (Gooch, 2002a).

In the 17th century the Dutch greatly increased availability of white lead and lowered cost. All white lead paints included chalk in their undercoats, reserving purer white lead for finish coats (Buxbaum, 1998).

The pigment industry started in the 18th century with products such as Berlin blue, cobalt blue, Scheele's green and chrome yellow.

In the 19th century, ultramarine, cobalt pigments, iron oxide pigments and cadmium pigments were developed in quick succession (Buxbaum, 1998).

In the later part of the twentieth century, society's growing environmental awareness has presented a new challenge to the paint and coatings industry to produce coating products that meet the demands of manufacturers and consumers and at the same time comply with the government environmental constraints. Certain chemicals have been shown to be toxic and hazardous to humans and their environment. Regulatory agencies are setting strict standards with which coatings manufacturers need to comply. This has led to a greater interest in developing coatings such as those that use water instead of volatile organic compounds in their formulation and powdered coatings that are absolutely solvent-free (Lambourne and Strivens, 1999).

1.1.2. Composition of paints

All paints are basically similar in composition, in that they contain a suspension of finely ground solids (pigments) in a liquid medium (vehicle) consisting of a polymer or resinous material (binder) and a volatile solvent.

A paint is formulated as a mixture of four ingredients: (1) Binder, (2) Solvent, (3) Pigment , (4) Additives (Ali, 2005).

1.1.2.1. Binder

The binder or resin forms the matrix of the coating, the continuous polymeric phase in which all other components can be incorporated. The resin is the film forming agent of the paint. Its density and composition are primarily responsible for determining the permeability, chemical resistance and ultraviolet (UV) resistance of the coating (Philip and Schweitzer, 2006).

There are numerous types of binders currently available to the paint industry for various applications such as alkyds, polyesters, acrylics, vinyls, natural resins and oils (Ali, 2005).

In most cases, binders produce the greatest volume of paint film and have the greatest influence on the paint characteristics (drying, adhesion, hardness, strength, resistance to chemicals, etc.). Therefore, the type of binder is generally used to describe the generic type of paint (Talbert, 2008).

1.1.2.2. Solvent

The main purposes of the solvent are to adjust the curing properties and viscosity of the paint. It is volatile and does not become part of the paint film. It also controls flow and application properties, and affects the stability of the paint while in liquid state.

Its main function is as the carrier for the non-volatile components. In order to spread heavier oils (i.e. linseed) as in oil-based interior house paint, thinner oil is required. These volatile substances impart their properties temporarily once the solvent has evaporated or disintegrated, the remaining paint is fixed to the surface (Tsegaye, 2011).

1.1.2.3. Pigments

Pigments are fine solid particles dispersed in the binder. Pigments provide color, gloss and opacity required of the paint film. Some pigments also act as protective agents against corrosion by atmospheric agents (Mateo, 2005).

Pigments, which can be organic or inorganic in origin, have been classified in a variety of ways, such as: color, natural or synthetic and by chemical types (Philip and Schweitzer, 2006).

The amount of pigment used is characterized by the pigment volume concentration (PVC), which is defined as (Carr, 2005).

$$\text{PVC} = \frac{volme\ of\ pigment}{volume\ of\ pigment\ and\ binder} \times 100\%$$

Metallic pigments such as aluminium, Zinc, copper alloys, stainless steel etc. anti corrosive pigments such red lead, silicon chromate, zinc and strontium chromate white molybdates, calcium plumbate etc. Functional and miscellaneous pigments such as cuprous and mercuric oxides, barium meta borate nacreous luminescent etc.(Tsegaye, 2011).

1.1.2.4. Additives

Additives are chemicals used in coating formulations to impart specific physical or chemical properties to the coating (Waters, 1996). Additives are various chemicals, typically added in small amounts, which can greatly affect the properties of a coating. These include surfactants, antisettling agents, coalescing agents, antiskinning agents, catalysts, defoamers, ultraviolet light absorbers, dispersing agents, preservatives, driers and plasticizers. Some chemists, however, would not consider a plasticizer to be an additive since sometimes they constitute a major ingredient of the formulation (Weldon, 2009).

These additives are usually added at small (less than 1%) levels, but can have a significant impact on the coating system (Philip and Schweitzer, 2006 and Weldon, 2009).

1.1.3. Properties of paints

Paint films are formed determines many of the key properties of a paint film. Therefore, paints are often classified according to their film formation characteristics. In general terms, paints can be divided into two categories:

Physically drying paints and chemically drying paints

In the physically drying paints, the binder molecules in the dry paint film are already present in the wet paint. There is no change in binder composition or molecule structure and size. The paint film is formed entirely by evaporation of solvents, thus leaving the binder molecules as chains coiled up and intertwined in the coating (Marrion, 2004).

In chemically drying paints, the final binder molecules in the dried paint film are not present in the wet film. The smaller "wet" molecules react chemically during and after application, thus creating new, larger binder molecules. Consequently, the film is formed by crosslinking of the molecules, and often by the evaporation of its solvents as well (Sward, 1972 and Marrion, 2004).

1.1.4. Classification of paints

There are different ways to classify paint materials based on their formulations (Talbert, 2008).

1.1.4.1. Solvent-borne paints

Solvent-borne paints contain up to 80% of solid constituents (binders, pigments and additives) dispersed in the organic solvent. Solvent-borne paints dry fast and may contain a wide range of binders. The main disadvantages of the solvent-borne paints are their toxicity and combustibility (Lambourne and Strivens, 1999).

1.1.4.2. Water-borne paints

Water-borne paints contain water as the paint solvent. Waterborne paints are non-toxic and non-combustible but they are characterized by long drying time due to slow evaporation rate of water.

- **Water-borne paints based on water-soluble binders** contain low molecular weight polymeric binders dispersed in water in form of true solutions. Water-soluble binders contain up to 15% of organic oxygen containing solvents soluble in water (alcohols, glycol ethers, etc.).
- **Water-borne paints based on polymer dispersions (Emulsion paints)** contain 50-60% of high molecular weight polymeric binders dispersed in water in form of Colloids. Emulsion paint contain up to 5% of organic oxygen containing solvents soluble in water (alcohols, glycol ethers, etc.) (Buxbaum, 1998 and Ali, 2005).

1.1.4.3. Powder paints

Powder paints are obtained from powdered resin, particles of which are attracted by the electrostatic force to the substrate surface. No solvent is involved in the process therefore powder coatings produce no/low toxic waste. The main disadvantage of powder coatings is high cost of equipment (Gettens and Stout, 1966; Sward, 1972 and Tracton, 2006).

1.2. Pigments

Pigments are inorganic or organic substances that are insoluble or substantially insoluble in water or the organic medium in which they are used as dispersions. They impart color, opacity, mechanical rigidity and reinforcement to the continuous phase in which they are dispersed.

Paint is a fine dispersion of pigments in binder in the presence of solvent and a small amount of additives. The final properties of the paint or coating depend on the properties of the binder, pigments or also on the additives. Pigments alter the appearance of the coating by selective absorption or by scattering of light. Pigments are classified on the basis of their performance as decorative pigments and protective pigments. Pigments also impart certain special properties to the coatings such as reflection of infrared radiation (Bendiganavale and Malshe, 2008).

1.2.1. History of pigments

Natural inorganic pigments have been known since prehistoric times. Over 60000 years ago, natural ocher was used in the Ice Age as a coloring material. The cave paintings of the Pleistocene peoples of southern France, northern Spain, and northern Africa were made with charcoal, ocher, manganese brown, and clays, and must have been produced over 30000 years ago (Buxbaum *et al.,* 2006).

In 1704 the first inorganic pigment was synthesized. It was not until a century later that the nard produced his blue. Ever increasing expertise and technology led to the production of chrome yellow, cadmium cobalt yellow, several synthetic iron oxides covering parts of the ranges of yellow, red, and black hues; chrome oxide green and ultramarine (Herbst and Hunger, 2004).

In the 19th century, ultramarine, Guignet's green, cobalt pigments, iron oxide pigments, and cadmium pigments were developed in quick succession (Buxbaum, 1998).

In the 20th century, pigments increasingly became the subject of scientific investigation. In the past few decades, the synthetic colored pigments cadmium red, manganese blue, molybdenum red, and mixed oxides with bismuth came onto the market. Titanium dioxide with anatase or rutile structures, and acicular zinc oxide were introduced as new synthetic white pigments and extenders, respectively (Buxbaum, 1998).

1.2.2. Properties of pigments

In general the following properties of the pigments are important in selecting a pigment for any particular product (Ali, 2005).

1.2.2.1. Tinting strength

Tinting strength of a coloured pigment is its ability to absorb the incident light and confer colour to the medium in which it is embedded. The tinting strength is an indication of a colouring material (Oyarzuun, 2000).

The majority of paints contain white pigment, which is tinted to the appropriate shade with colored pigments. If a lot of colored pigment is required to achieve the shade, it is said to have tinting strength and vice versa (Ali, 2005).

1.2.2.2. Light fastness

Light fastness of a paint is its ability to resist deterioration under the action of sunlight and industrial fumes. Pigment stability during exposure to sunlight and environment is of considerable importance. Many pigments fade or darken or change shade badly in the light. This is because the ultra-violet rays in the sunlight are sufficiently energetic to break certain chemical bonds and thus change molecules (Ali, 2005).

1.2.2.3. Hiding Power

The hiding power is the important property of a pigment, when made into paint, to obscure the surface on which it is applied. The definition of hiding power is based on a black and white contrasting support upon which the film of coating is applied (Getens and Stout, 1966).

In the case of white pigments, the ability to reflect light and obscure black is the measure of hiding power of a pigment is proportional to its refractive index, to fineness of particle size and to depth of colour (Völz, 2006).

1.2.2.4. Particle size

The particle size affects the hiding power of the paints (Ali, 2005). Particle size may be regarded relatively as very fine, fine, medium, large, coarse, the standard unit of measurement is the micrometer (Eastaugh *et al.*, 2004). The finer the pigment particle the greater the hiding power of the paint. Fine grinding is also necessary to provide smoothness in the paint film, which is especially sought in enamels and machinery paints (Ali, 2005).

1.2.2.5. Particle shape

Particles may be nearly spherical, cubic, nodular (a rounded irregular shape), acicular (needle or rod-like) or lamellar (plate-like). Since particle shape affects pigment packing, it therefore affects hiding power.

Rod-shaped particles can reinforce paint film, like iron bars in concrete, and they may tend to poke throughout the surface reducing gloss. Such rough surfaces may help the next coat to stick more easily, so this type of pigment could be useful in an undercoat.

Plate-shaped particles tend to overlap one another like tile on a roof, making it more difficult for water to penetrate the film. Aluminium and mica pigment have this shape (Ali, 2005).

1.2.3. Classification of pigments

Pigments are organic or inorganic colorants that are used in the form of insoluble powders. Today, the use of pigments is widespread and includes coating technology, paints, inks and plastic coloration as well as relatively new technologies such as information storage systems (Smith, 2002).

1.2.3.1. Inorganic pigments

Inorganic pigments include white opaque pigments used to provide opacity and to lighten other colours. The most important member of the class is titanium dioxide. White extender pigments are added to paints to lower their cost or improve their properties. This class includes calcium carbonate, calcium sulfate, diatomaceous silica (the remains of marine organisms), and china clays. Black pigments are primarily created from particles of carbon. Carbon black for example is used to give black colour to printing inks. Certain compounds of chromium are used to provide chrome yellows, oranges, and greens, while various compounds of cadmium yield brilliant yellows, oranges, and reds. Iron, or Prussian, blue and ultramarine blue are the most widely used blue pigments and are both inorganic in origin (Sward, 1972 and Buxbaum, 1998) .

1.2.3.2. Organic pigments

Organic pigments have less durability and fewer lasting qualities than the inorganic pigments. Pigments used in modern painting are usually made synthetically. One natural organic pigment is coal black, which is made of charcoal, preferably from willow, beech and maple. Organic pigments are not normally used nowadays for painting buildings, with the exception of some blue and green variations (BjØrn, 2001).

Organic pigments have a high light absorption and a low scattering power, whereas inorganic pigments have a low light absorption and high scattering power. Combinations of organic and inorganic pigments are therefore often advantageous. Organic pigments are therefore often advantageous. Organic pigments also have a lower density and higher surface area than inorganic pigments; their color purity and tinting strength are often higher. Organic pigments tend to dissolve at high temperature and in binders and solvents (Stoye and Freitag, 1998).

1.2.4. Inorganic colour pigments

1.2.4.1. Inorganic yellow pigments

The chrome yellow pigments are pure lead chromates or mixed-phase pigments of lead chromate and lead sulphate with the general formula $Pb(Cr,S)O_4$. Molybdate red and molybdate orange are mixed-phase pigments of lead chromate, lead sulphate and lead molybdate with the general formula $Pb(Cr,S,Mo)O_4$.

Lead chromate pigments ($PbCrO_4$) and chrome yellow (mixtures of lead chromate and lead sulfate) are available in a wide range of hues (Hare, 1994). Lead chromate pigments are used for colouring paints and plastics, and are characterised by brilliant hues, good tinting strength and hiding power. Special treatment of the pigments with silicates and antimony compounds has allowed continuous improvement of their resistance to light, weathering, chemicals, and temperature (Völz, 2006).

They are synthetic pigments that range in colour from yellow through primrose to orange. They are heat resistant, lightfast and alkaline resistant, but have poor acid resistance. Although a very useful pigment, there is some concern about the toxic effects of cadmium (Hare, 1994).

1.2.4.2. Inorganic green pigments

The most widely used inorganic green pigment is chromium oxide (Cr_2O_3), also known as chromium green oxide. This is a dull green synthetic pigment that has good stability to heat, light, acids and alkalis, is relatively inexpensive and has good opacity (Weldon, 2009).

Chromium oxide green is rare as a single compound (Cr_2O_3) green pigment, whereas many inorganic greens are a mix of yellow and blue pigment materials. It is a pigment insoluble in water, acid or alkalai and thus stable when exposed to sulphur dioxide and when applied to or mixed in concrete (Buxbaum, 1998).

The use of chromium (II1) oxide as a pigment for toys, cosmetics, and in plastics and paints that come in contact with food is permitted in national and international regulations (Buxbaum, 1998).

1.2.4.3. Inorganic red pigments

Pigment red is cadmium sulfoselenide red, a solid solution of cadmium sulfide and cadmium selenide produced by a co precipitate of cadmium sulfide and cadmium sulfoselenide. The amount of cadmium selenide incorporated into the solid solution dictates the final hue of the pigment as does also, to a lesser extent, the temperature of calcinations. The empirical formula is CdS . xCdSe (Tracton, 2006).

Red lead (Pb_3O_4) is a brilliant red-orange colored synthetic inorganic pigment used mainly as a protective priming coat for steel work rather than a coloring pigment in paints. The toxic nature of this pigment restricts its use in modern coating systems (Ali, 2005).

1.2.4.4. Inorganic Blue Pigments

Ultramarine blue. This color, sometimes known as cobalt blue, is popularly used as a tinting color. It gives an attractive reddish cast when added to whites. Ultramarine blue has poor opacity, high heat resistance, and good alkali resistance. Although it can be used in latex paints, special grades low in water-soluble salts must be obtained. It is often used for whites to give extra opacity and make them look whiter by lending them a bluish cast (Gooch, 2002b).

Iron blue also known as Prussian Blue, this pigment is manufactured by reacting ferrous sulfate and sodium ferrocyanide in the presence of ammonium sulfite to yield a leucoferricyanide called Berlin White, which is then isolated and dissolved in sulfuric acid and oxidized with sodium chlorate to yield iron blue. Iron blue pigments are used in the paint industry, especially for full, dark blue colors for automotive finishes. (Buxbaum, 1998).

1.3. Health hazards of paint and pigments

Paint contains pigments, solvents, resins and other ingredients to give it color, texture, spread ability and durability. Many of these ingredients are hazardous to your health. First among them are the solvents, such as mineral spirits, naphtha and turpentine, that evaporate readily from paint exposed to the air.

Even short-term exposure to these chemicals can cause dizziness, eye irritation, nausea, coughing and other symptoms. In addition, paints containing polyisocyanate hardeners can cause shortness of breath, chills and fever.

Long-term exposure to paint ingredients, even when no short term effects are noticed, can damage the kidneys, liver, blood or nervous system. Some even cause cancer and birth defects in laboratory animals. Paints for a long time with no ill effects. Suddenly you develop rashes, hives, swelling or scaling of the skin, or you begin coughing and having shortness of breath, which often leads to permanent lung damage or severe respiratory stress (Piper, 1965 and U.S.APHC, 2012)

1.4. Trace metals

1.4.1. Definition is paints and pigments

Trace elements constitute a natural component of the earth crust. They are not biodegradable, hence persist in the environment (Abolude *et al.*, 2009). Heavy metals are a group of elements with a mass density greater than 4.5 g/cm^3 (Szyczewski *et al.*, 2009).

The elements present only in trace concentrations in the human body but still having a well-defined biochemical function are chromium, cobalt, copper, iodine, iron, manganese, molybdenum, selenium and zinc (Steinnes, 2010).

Heavy metals can pose health hazards to man and aquatic lives if their concentrations exceed allowable limits. Concentrations of heavy metals below these limits even have potential for long-term contamination, because heavy metals are known to be accumulative within biological systems (Malakootian *et al.,* 2008).

These trace elements are found in concentrations less than a thousand parts per million; most are under one hundred parts per million (Conaway, 2001).

1.4.2. Trace elements in the environmental

Trace metals are important environmental pollutants that are a threat to the health of human populations and natural ecosystems (Premarathna *et al.*, 2011).

Small amounts of these elements are common in our environment and diet and are actually necessary for good health, but large amounts of any of them may cause acute or chronic toxicity (poisoning). 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. 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 cause cancer (CIS, 1999).

Environmental pollution and continuous exposure of human beings to toxic heavy metals such as mercury, cadmium and lead is a seriously growing problem throughout the world. Exposure to metals has risen dramatically in the last fifty years as a result of an exponential increase in the use of heavy metals in industrial processes and products (Premarathna *et al.*, 2011).

1.4.3. Sources and toxicity of selected trace heavy metals

The heavy metal content of sediments comes from natural sources (rock weathering, soil erosion, dissolution of water-soluble salts) as well as anthropogenic sources such as municipal wastewater-treatment plants, manufacturing industries, and agricultural activities etc (ERDOĞAN, 2009). Heavy metals are mainly used as pigments and blotters in the paint. The presence of these heavy metals are directly and indirectly hazardous for human and other beings (Clark, 1972 ; Nergo, 1993 and Malakootian *et al.*, 2008).

The toxicity of heavy metals has long been concerned since it is very important to the health of people and ecology (Sanayei *et al.*, 2009). Children may develop toxic levels from normal hand-to-mouth activity (Dupler, 2001).

The elements Cd , Cr and Pb are all naturally occurring substances which are often present in the environment at low levels. In larger amounts, they can be dangerous. Toxicity from these heavy metals can lead to damaged or reduced mental and central nervous systems function, lower energy levels, damage to blood composition, lungs, kidneys, liver and other vital organs (Amartey *et al.*, 2011).

1.4.3.1. Lead

Many sources of lead exposure affect the workplace and the general population (Bolt, 2005). Drinking water can be a significant contribution to lead intake, especially for young children. Lead can enter the human body through the skin, by inhalation in paints, or by ingestion. Ingestion in food is generally the major source of lead intake. Lead in the diet can come from numerous sources such as uptake of lead into plants; deposition onto vegetables; from soil or water; and from lead solder in canned goods (U.S. EPA, 1993). Pb from gasoline and paint can remain in soil and dust for many years (Hepp *et al.*, 2009).

Lead has toxicity effects to human health (Jakmunee *et al.*, 2001). Lead has special industrial significance since it is employed in batteries, paints, pigments and ammunition, petrol, cables, alloys and steels, plastics, the glass industry and the metal industry (Selatnia *et al.*, 2004).

Lead is known to cause serious conditions such as anemia, brain damage and kidney failure because of size and charge similarities, lead can substitute for calcium and included in bones; children are especially susceptible to this effect (Sasi, 2005).

Chronic effects are more diffuse but include disruption of the neural system, the kidneys and the blood production (Selander and Svan, 2007).

Pubic health awareness of the dangers to the health of children and others from lead-based paint increased in the United States in the middle of the 20th century, although a US regulation of the lead content in new paint for residential use was not in effect until 1978 when a limit of 600 ppm became effective (CPSC, 1977). For existing housing, US regulations now require that the paint contain less than 5000 ppm or 1.0 mg/cm2 of lead (HUD, 1995 and U.S. EPA, 2001).

In Australia recommended 0.1% percent of total lead as the maximum amount of lead in domestic paint (DEH, 2001). Singapore has a standard of 0.06% in new paints. In China the standard is 90 ppm (Barboza, 2007).

1.4.3.2. Cadmium

Cadmium is a byproduct of the mining and smelting of lead and zinc. It is used in nickel-cadmium batteries, PVC plastics, and paint pigments. It can be found in soils because insecticides, fungicides, sludge, and commercial fertilizers that contain cadmium are used in agriculture (Eshun, 2011).

Cadmium is one of the toxic elements (Hu *et al.*, 1992). This element is widely used in industry, especially in electroplating, pigments for paints, enamel, glass, plastics, printing inks, rubber and lacquers, alloys, in the production of Ni–Cd batteries, as stabilizer in thermoplastics, for photoconductors and photoelectric solar cells, automobile tires and control rods in nuclear reactors. Food and cigarette smoke are the main sources of cadmium exposure for the general population. There are indications that the occurrence of this metal in foodstuffs has increased as a result of contamination of the environment (ATSDR, 2012). Cadmium is a relatively volatile element not essential to plants, animals and humans (Šmirjákova, *et al.*, 2005).

Cadmium is an important environmental constituent widely used in industrial processes for production of synthetic materials and therefore can be released in the environment causing public exposure especially around the industrial residence area (Shahtaheri *et al.*, 2006).

In the European Economic Community, the following limits for the pigment production must be observed: 0.2 mg Cd/L in wastewater and 0.3 kg Cd per tonne of used cadmium compounds, calculated as metal.

In Germany, the following maximum BAT values are permitted in the workplace: 15 µg Cd per liter urine and 1.5 µg Cd per 100 mL blood. The TRK value for cadmium pigments is 0.015 mg/m^3.

In the United States, the TLV value for cadmium and its compounds is 0.01 mg Cd/m^3 (Buxbaum *et al.*, 2006).

1.4.3.3. Chromium

Chromium is an element occurring in food products of both plant and animal origins. It is regarded as an essential trace element in humans and animals, taking part in various metabolic processes. Chromium, as an essential element is usually present in food in the trivalent form; the hexavalent form of chromium is toxic and not normally found in food (Rêczajska *et al.*, 2005).

Blue prints, primer paints, household chemicals and cleaners, cements, diesel engines utilizing anti-corrosive agents, upholstery dyes, leather tanning processes, welding fumes, battery, rubber, dye, candles, printers and matches are occupational and environmental sources of chromium (Koplan, 2000).

People may also be exposed to higher levels of chromium if they use tobacco products, since tobacco contains chromium. Workers in industries that use chromium are one segment of the population that is especially at high risk to chromium exposure. Occupational exposure from chromate production, stainless steel welding, chromium plating, and ferrochrome and chrome pigment production is especially significant since the exposure from these industries is to chromium (VI) (U.S. EPA, 1984).

The major toxic effects of chromium are chronic ulcers, dermatitis and corrosive reaction in nasal septum and local effects in lungs (Maria *et al.*, 2009).

The employer must determine each employee’s 8-hour, time weighted average (TWA) exposure to Cr (VI). Monitoring results must be compared to the permissible exposure limit (PEL) of 5 micrograms per cubic meter of air (5 $\mu g/m^3$), and the Action Level of 2.5 $\mu g/m^3$ (OSHA, 2006).

1.4.4. Transport heavy metal in the environmental

Heavy metals are released into the environment by many human activities. They are also used in a large variety of industrial products, which in the long term have to be deposited as waste. Heavy metal release into the environment occurs at the beginning of the production chain, whenever ores are mined, during the use of products containing them, and also at the end of the production chain (Manahan, 2000).

The environmental problems with heavy metals are that they as elements are undestroyable and the most of them have toxic effects on living organisms when exceeding a certain concentration. Furthermore, some heavy metals are being subjected to bioaccumulation and may pose a risk to human health when transferred to the food chain (Sherene, 2010).

1.5. Related work done in the region and around the world

Determination the levels of heavy metals in oil paint and pigment samples have received considerable attention in different countries in the region the world. Some of the important documented contribution related to the present study are as follows:

George Foundation selected 24 paint samples from six paint companies purchased in stores in Bangalore and Chennai. The 24 samples analyzed, 17 had lead concentrations exceeding 0.5% lead by weight, 13 had lead concentrations exceeding 1% lead and 5 exceeded 10% lead. On the basis of a two coat paint thickness, the XRF determination of paint lead loading exceeded 1 mg/cm^2 in five of the samples. The lower Pb concentration paints are the white, blue and brown-red paints, while in order of increasing Pb concentrations are the green, red, orange and the yellow paints (Van Alphen, 1999).

Another study in USA ,determination of Ti, Zn, and Pb in lead-based house paints by EDXRF from five different manufacturers. Although the relative concentrations of several elements in the paints were determined, the three element combinations of Ti, Zn, and Pb proved to be very successful in discriminating between the different manufacturers of paint. Results indicated the concentration were below the maximum permissible levels according to American Society for Testing Material (ASTM) (Hall and Tinklenberg, 2003).

Yellow paints showed highest lead levels as compared to others. Yellow paint pigments containing 200,000 ppm of lead were obtained as samples in paint manufacturing facilities and in an academic paint technology department. Yellow-derivative paints (green and brown) had the next highest amount of lead. After a third coat, the red paints also exceeded the given standard of 1.0 mg/cm2 (Clark *et al.*, 2005).

A survey was conducted by the South African Medical Research Council of the lead concentrations in paint samples collected from dwellings located in randomly selected Johannesburg suburbs. Of the 239 dwellings included in the survey, 20% had paint lead concentrations > 5,000 µg/g (the U.S. reference level). Paint with high lead levels was found in old as well as newly constructed dwellings (Montgomery and Mathee, 2005).

Nineteen samples of locally manufactured paints purchased from the Nigerian market in February, 2005 were analysed for lead. The level of lead in the paints ranged from 17.5 µg/g to 515.9 µg/g with mean standard deviation of 62.2µg/g (115.1µg/g), while the median was 25.1µg/g. It was concluded that paints sold in Nigeria contain a substantial amount of lead with increased risk of exposure to children, for whom domestic sources of lead exposure is more important than exposure through leaded petrol (Adebamowo *et al.*, 2006).

From a total of 80 paint samples obtained from China, India, and Malaysia – 66% of new paint samples were found to contain 5000 ppm (0.5%) or more of lead, the US definition of lead based paint in existing housing, and 78% contained 600 ppm (0.06%) or more, the limit for new paints. In contrast, the comparable levels in a nearby developed country, Singapore, were 0% and 9%. An examination of lead levels in paints of the same brands purchased in different countries showed that some brands had lead-based paints in one of the countries and paints meeting US limits in another; another had lead-free paint available in all countries where samples were obtained. Some brands of paint marketed in two or more countries had lead based paint in one country and low lead based paints in the country that had a regulatory limit. They also reported that 100 percent (n=17) of paint samples from India had more than 600 ppm of lead concentration while 82% samples had more than 5000 ppm of lead contents (Clark *et al.*, 2006).

Another study on lead levels of paints (5 colours) manufactured in Nigeria the lead was measured by flame-atomic absorption spectroscopy. It was found that 96% of the paints had higher than recommended levels of lead. The mean lead level of paints ranged from 84.8 to 50,000 ppm, with a mean of 14,500 ppm and median of 15,800 ppm. The main determinant of lead levels was the color of the paint.
The study concluded that efforts need to be undertaken to assess the presence of high lead levels in existing housing and if detected, intervention programs for eliminating risk of exposure should be developed in addition to measures to increase awareness and enforce regulations leading to the elimination of lead based domestic paint (Adebamowo, 2007).

In a study performed by Mohammed et al., Elemental analysis composition of most common paint present in the Saudi Arabian market were produced by three different companies and classified according to paint types. Therefore, six sets of different color paint sample were analyzed to determine their element composition. The color of water-based paint and the oil-based paint are obtained by automatic addition of small doses of different liquid of pigment to the base paints. The pigment doses and their mixing with the bases are made by machine controlled by computer to obtain the desired colors. Two extra sets of different pigments ingredient, collected from the products of the local company and the European company, were also analyzed. They showed result that the concentration trace elements less than 0.5% while in pigment ingredient of all seem lead free that indicates. The oil based paints analysis shows less than 0.5%, the result were exceeding the permission limit allowed by environmental protection agency (EPA*)* (AL Eshaikh and Kadachi, 2007).

In study on determination of trace elements in paints by direct sampling graphite furnace atomic absorption spectrometry (DS-GFAAS), They found the limits of detection were 0.0004, 0.001, 0.03, 0.22, 0.11 and 0.05µg/g of Cd, Pb, Cr, Ni, Co and Cu, respectively. The accuracy was determined by comparison of the results with those obtained by inductively coupled plasma mass spectrometry (ICP-MS) and graphite furnace atomic absorption spectrometry (GFAAS). The results obtained indicate the potential of the developed method for trace elements determination in small amounts of sample, which may also be useful in forensic and archeometry investigations (Bentlin *et al*., 2007).

A study on lead in paints in India conducted by Toxics Link and entitled "Brush with Toxics" studied different types of paints. Lead content was found to be high up to 140,000 ppm in many oil based enamel paints. Concentrations of lead in 83.87 % of the enamel paint samples were found to be more than 1000 ppm and 61.3% of samples had more than 5000 ppm. The colour of the paint was related to lead content. While yellow and orange coloured paints had the highest concentrations of lead, black and white showed the lowest concentrations (Kumar, 2007).

Paint samples purchased from Johannesburg and Cape Town stores were analyzed for lead content. No lead was found in water-based or white shades of enamel paint, alarmingly high lead concentrations (up to 189,000 µg/g) were measured in samples of pigmented enamel paints. A total of 83% samples of pigmented enamel paints were lead based. High lead concentrations were found in popular as well as lesser-known brands of enamel paint, and only 2 out of 25 samples of lead-based paint displayed warnings of the high lead content. Similarly high lead concentrations (up to 145,000 µg/g) were found in paint removed from widely used children's toys (such as building blocks) that were purchased from 7 major toy, supermarket, and stationery chain stores as well as flea and craft markets. High lead levels were found in locally manufactured as well as imported toys (Mathee *et al.*, 2007).

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology in China, Determination of cadmium in paint five samples by graphite furnace atomic absorption spectrometry were provided by different manufactures. All the samples examined were used to coat woodworks. They found the concentration of cadmium in examined were significantly lower than the current established tolerance of 75 mg/kg of dissolved cadmium in solvent coatings for woodenware by Chinese national standard (Wang *et al.*, 2007).

In their study to determination of lead in 36 samples of white water based paint of Libyan products, the results showed that the average concentration of lead between (0.201 mg/l-1.510 mg/l) and has lead percentage between (0.043% -0.189%). Also, have different lead conc. in two serial numbers. This mean that these was not based on the Libyan paint standard specification, which depended on the ISO, BSI, ASTM, HUD and EPA international paint standards specification, which state that the paint must be free of lead (El-Atrash and Benghuzzi, 2008).

In study for lead content in household paints in India, 69 paint samples were purchased from retail shops in Delhi and Mumbai in November and December 2006 and brought to the Toxics Link office in Delhi. The selected paints were from six common brands readily available in the Indian market and samples were analyzed for total lead by Inductively Coupled Plasma Emission Spectroscopy. The study was undertaken to determine the levels of lead in new latex (water-based) and enamel paints (oil-based) intended for residential use in India. analyzed 38 new latex and 31 new enamel paint samples from India for lead content and found low levels in the latex paints, well below 600ppm and high levels in five of the six brands of enamel paints. The arithmetic average level in the enamel paints was 26,100ppm and the maximum was 40,000 ppm. The percentage of samples that were equal to or exceeded the limit of 600 ppm ranged from 33% (China) to 96% (Nigeria). The finding of high lead in new enamel paints for domestic use in India and China (Kumar and Gottesfeld, 2008).

In a report on the analysis for lead in new enamel household paints were collected from a total of 12 countries in Africa, Asia and South America and analyzed for lead in the Hematology and Environmental Laboratory at the University of Cincinnati The average concentration of lead in new enamel household paints in the countries in this study ranged from 6988 to 31,960 ppm. The percentage of samples that were equal to or exceeded the limit of 600 ppm ranged from 33% (China) to 96% (Nigeria). An average of 73% of the paint brands tested in the various countries had at least one sample with a lead concentration that was at least 600 ppm. Only a slightly smaller percentage had at least one sample with a much higher concentration, 10,000 ppm. Fifty- four percent of the paints tested in Singapore and China had concentrations less than 90 ppm indicating that the technology is available in these countries to produce low lead paints that would meet the new limit for new paints in the United States (Clark *et al.*, 2009).

This study was carried out to determine the total lead content in enamel paint in major paint companies in Bangladesh. Twenty five enamel paint samples (5 colours) were randomly purchased from various markets. The paint samples were purchased in Samples were analysed by Atomic Absorption Spectrometer using Air-Acetylene flame. Lead was found in all enamel paint samples tested. 96% (24 out of 25 samples) of the enamel paint samples did not meet the specification for lead content prescribed by US and China limit.

The average concentration of lead in all enamel paint samples ranged from 55 to 114010 ppm. Highest (114010 ppm) concentration of lead was detected in Golden yellow of Robbialac Acrylic Distemper manufactured by Berger paints which is 1267 times higher than the US and China limit for new paints (90 ppm). Lowest (55 ppm) concentration of lead was detected in white brand of paints manufactured by Pailac paints. The average concentration of lead for yellow enamel paints of all the five brands was 75286 ppm followed by orange which was 54708.2 ppm, green 28926 ppm, black 14967.2 ppm and finally white enamel paint contained 357.4 ppm. Formulation of a national policy on paint manufacture and its proper implementation is inevitable to stop the use of lead in paints in Bangladesh (Hossain *et al.*, 2013).

1.6. Related studies in effected heavy metals from paints

In 1997, determination trace elements contained in human hair of Fifty four hair samples from the workers of paint factory, including chromium, iron, lead, and manganese. The hair sample was pretreated with organic solvent and by microwave digestion before their trace metals were measured with Graphite Furnace System Atomic absorption spectrophotometers . Lead (8.2-26 µg/g,) and manganese (631.2 - 1521.7 µg/kg, concentrations in the hair from workers of the paint factory had higher than healthy controls, but iron concentration (28.2 - 90.7 µg/g) had lower than those of healthy controls. but the total. chromium level did not significant differ from that in normal control (TsAI *et al.*, 1997).

This study was granted by the Hi-Tech Research and Development Program and Zhejiang Provincial Natural Science Foundation in China**.** Total concentrations of heavy metals such as cadmium (Cd), chromium (Cr), nickel (Ni) and lead (Pb) in topsoil (0-30 cm). subsoil (30-60 cm), and basal-soil (60-100) in the site of a retired paint/ink manufactory of Soils. The results indicated that the soils collected in this survey were contaminated by Cd, Ni, Pb, and Zn, and chromium pollution in the soils was not apparent. Cd pollution in the soils were extremely serious. Cd concentrations in some soil samples were excessive to the maximum allowable limits (MAL), and the safe treatments of the soils represented by these samples is needed (Weichang *et al.*, 2012).

In Nigeria, analyzed the Soil, tomato leaves and fruits samples collected for the period covering May to October, 2011 in the vicinity of paint factory were analytically digested and analyzed for trace elements such as lead, cooper, cadmium, nickel, zinc, chromium, manganese, arsenic, iron, selenium and cobalt respectively. Using atomic absorption spectrophotometer . The results obtained revealed that all the aforementioned trace elements analyzed were detected and metal concentrations were varied except cadmium, arsenic and selenium with constant value for all the months (0.01mg/kg). This study is an indicator to monitor lead toxicity around industrial locations in Nigeria. Metals such as copper, cadmium, chromium, arsenic, selenium and cobalt levels are not attributed to the paint factory's activities, other factors such as anthropogenic wastes, soil leach ate mechanic workshops and geochemical activities may be responsible for their presence (Nwajei *et al.*, 2012).

1.7. Analytical techniques

1.7.1. X–Ray fluorescence (XRF) spectrometry

X–Ray fluorescence (XRF) spectrometry provides one of the simplest, most accurate and most economical analytical technique for the qualitative and quantitative determination of the chemical composition of a wide variety of matrices at major, minor and trace levels of abundance. It is universally recognized as a non–destructive method for rapid and sequential, or simultaneous analysis of elemental composition of a material. XRF is reliable and requires no, or very little, sample preparation (Hamilton, 1979 and Margui *et al.*, 2005).

The X–ray region of the electromagnetic spectrum lies between 0.1 and 100Å. XRF has the advantage of being non–destructive, multi–elemental, fast and cost–effective. Furthermore, it provides a fairly uniform detection limit across a large portion of the elements on the periodic table and is applicable to a wide range of concentrations. Its main disadvantage is that analyses are generally restricted to elements heavier than fluorine. In other words, it can be used for a wide range of elements, from sodium (11) to uranium (92), and provides detection limits at the sub ppm level; it can also measure concentrations of up to 100% easily and simultaneously (Bencomo, 2010).

1.7.1.1. General principles of XRF spectrometry

The principle of X-ray fluorescence is simple: when an X-ray emission from a radioactive source strikes a sample, the X-ray can either be absorbed by atoms or scattered through the material. After absorption the atoms becomes "excited" and give off a characteristic X-ray whose energy level is unique to the element impacted by the incident X-ray. The emission of these characteristic X-ray is called X-ray fluorescence, or XRF. Measurement of the discrete energy of the X-rays emitted is used to identify the metals species present; measurement of the number of emitted X-ray provides a quantitative indication of the concentration of the metal present in sample (Ulmanu *et al.*,2011).

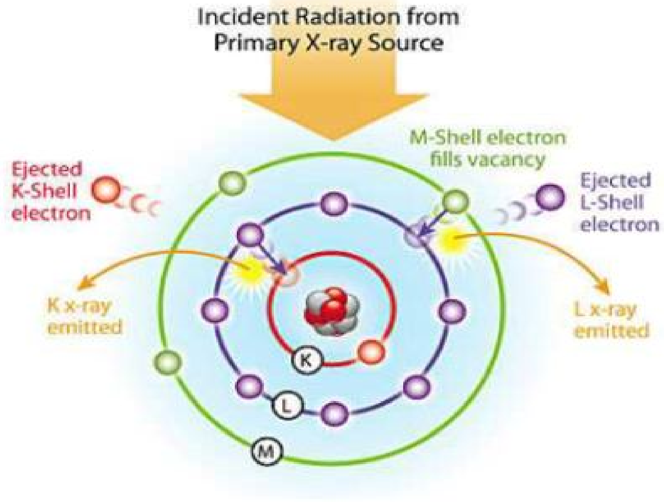

Figure (1.1): Physics of X-ray Fluorescence (XRF) Source: How xrf works. 2012

1.7.1.2. Types of XRF spectrometer

There are generally two types of XRF spectrometers: wavelength dispersive (WDXRF) and energy dispersive (ED-XRF). Wavelength dispersive system uses a diffraction crystal to focus specific wavelengths onto a detector. A wavelength range is scanned by changing the angle in which the X-rays strike the crystal. An energy dispersive spectrometer focuses all the emitted X-rays onto an energy analyzing detector (Havrilla, 1997).

Energy dispersive X-Ray Fluorescence (EDXRF) is a very attractive alternative for analyzing metals in both liquid and solid sample, often with minimal pretreatment.

EDXRF enables non-destructive, multi elements analysis to be done rapidly with high precision on a variety of sample types. Both qualitative and quantitative analysis may be done simultaneously. An X-ray spectrum is relatively simple as there are only a few lines for each element (Andrew, 2002).

Energy dispersive instrument is divided into X-ray sources or radioactive substance sources depending upon which sources depending upon which sources serve as a X-Ray Sources (Jenkins, 2000).

○ *X-Ray Source*

X-ray tubes, radio-isotopes and secondary fluorescence sources are the three source used in X-ray instruments

• The X-Ray Tube

The most common source of x-rays for analytical methods is the x-ray tube. The x-ray source is a tube under vacuum in which is mounted a tungsten filament cathode and an anode. The anode consists of a block of copper with metal target plated on the surface (Jenkins *et al.*, 1981). Figure (1.2) Shows a schematic cross-section of a sealed X-ray tube.

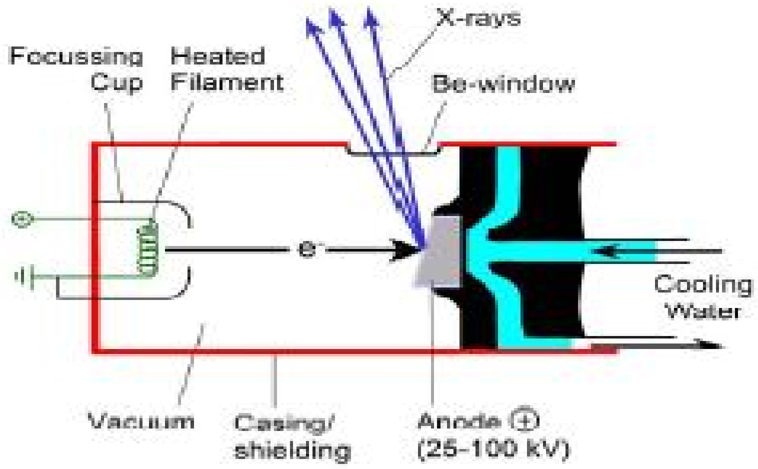

Figure (1.2): Shows a schematic cross-section of a sealed X-ray tube. Source: (Gauglitz and Vo-Dinh, 2003).

- **Radio-isotopes**

A number of radioactive substances are employed as sources in x-ray fluorescence methods. Many radioactive sources provide simple line spectra and others like $^{147}_{61}\mathrm{Pm}-\mathrm{Al}$ produce a continuous spectrum (Potts, 1995).

- **Secondary Fluorescent Sources**

Fluorescent spectra of elements that are excited by radiation from an x-ray tube can serve as a source of absorption of fluorescence. This is known as a secondary Fluorescence source.

- ***X-Ray Detectors***

X-ray detectors convert energy into an electrical signal. Three types of detectors are used for x-ray methods. They include gas-filled detectors, scintillation counters and semi-conductor detectors (Kenkel, 2003 and Patnaik, 2004).

1.7.1.3. Detection limits

X-ray fluorescence methods are generally not as sensitive as optical methods. In most cases, concentrations of a few part per million can be measured. X-ray fluorescence spectra are relatively simple which implies that spectral line interferences are unlikely. Generally, X-ray fluorescence methods are used on a variety of objects without destruction of the sample. Analyses are also performed on samples ranging from a barely visible speck to a massive object. X-ray fluorescence is used to measure major metal content of many different samples. It is also applied to measure trace metals in samples (Patnaik, 2004).

1.7.1.4. Quantitative and trace element analysis using XRF

Qualitative analysis is in principle very simple with XRF and is based on the accurate measurement of the energy, or wavelength, of the fluorescent lines observed (Grieken and Markowicz, 1993).

XRF is applicable to the qualitative and quantitative determination of low concentrations of elements in a wide range of samples and to the analysis of higher concentrations in small amounts of sample (Jenkins *et al.,* 1981).

1.7.2. Graphite furnace atomic absorption spectrometry (GFAAS)

Graphite furnace atomic absorption spectrometry (GFAAS) is a type of atomic absorption spectroscopy (AAS) that allows for identification and quantification of elements within aqueous samples. AAS is based on electron transitions between energy states of an atom. At room temperature, electrons are in the lowest energy state, which is called the ground state. When external energy is applied to the atom, an outermost valence electron can absorb the energy and become excited and this causes it to move into a higher energy level. Figure(1.3) Shows an example of a valence electron being excited into a higher energy level (Dean, 1997 and Welz and Sperling, 1999).

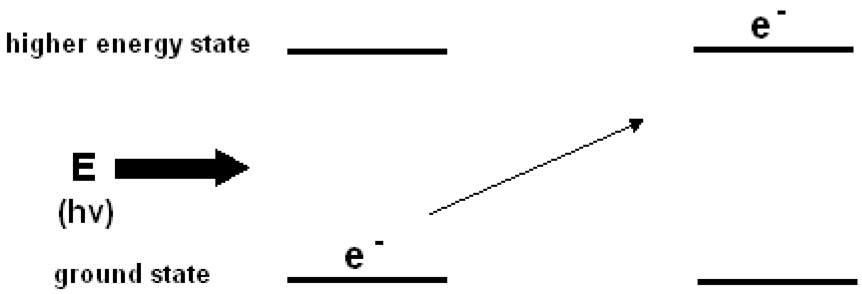

Figure (1.3): Example of a valence electron being excited by external energy (light in this case) and moving into a higher energy level.

The spacing between energy levels corresponds to the wavelength of radiation and this relationship is shown in equation 1.

$$E = \frac{hc}{\lambda} \qquad \text{(eq. 1)}$$

The energy that is absorbed is E (J), h is Planck's constant, c is the speed of light (m/s), and λ is the wavelength (m). Because each element requires a different amount of energy to excite the valence electron, a unique spectrum is observed based on the different wavelengths of light that are absorbed (Dean, 1997 and Welz and Sperling, 1999).

To achieve better element selectivity and reduce excess signals during analysis, a common external energy source is a line source that emits only the wavelengths that are absorbed by the element(s) of interest. The most favored line sources are hollow-cathode lamps (HCL), which contain vapor of the same element being analyzed (Dean, 1997 and Harris, 2003).

Once the sample absorbs a portion of the external energy, the remaining intensity of wavelengths are passed through a monochromator, which is a device for narrowing the range of wavelengths that are to be detected during analysis. A monochromator has slits that allow only certain wavelengths of light from the sample to reach the detector.

The combination of a hollow-cathode lamp and a monochromator allows for wavelength selectivity and hence excellent elemental analysis (Harris, 2003).

Instruments for AAS contain an external energy source, an atomization cell, means of wavelength selection, and a detector, as shown in Figure (1.4) (Dean, 1997).

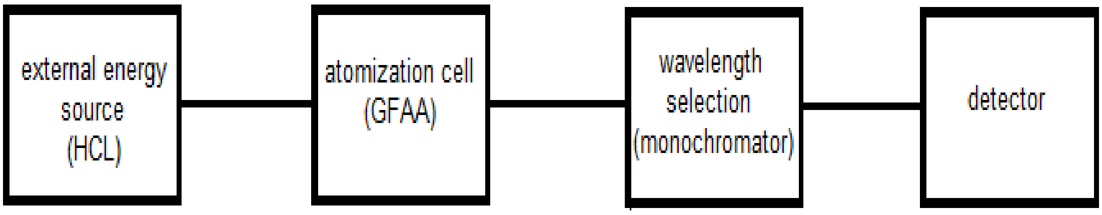

Figure (1.4): General diagram of the scheme of an atomic absorption spectrometer.

A small volume of sample (1-100 µL) is mechanically injected through a small hole in the side of the tube and light from the external energy source passes through the length of the tube. The graphite tube is heated electrically to higher and higher temperatures at specified time intervals in order to efficiently atomize the sample inside. The first temperature step (~ 125 °C) is to evaporate any solvent that may be present. The second step is called charring and is near 1400 °C to eliminate any organic matter. Then the atomization step occurs above 2000 °C (but not to exceed 2700 °C) for about 10 s and the absorbance is measured. Then the temperature is increased further (again, not to exceed 2700 °C) to clean the tube to prepare for another sample to be injected. Atomization by graphite furnace is a sensitive technique because the sample is contained within the graphite tube so more atoms are kept in the path of the energy source while measurements are made. The greater the number of atoms within the path of the light source, the more sensitive the analysis of the sample (Harris, 2003).

1.7.2.1. Quantitative and trace element analysis using GFAAS

Graphite furnace AA exists in the modern trace metal arsenal as a reliable and rugged analytical tool. With modern use of the technique, high precision (3–5% relative standard deviation) and accurate results can be obtained on a routine basis. With low parts per billion for relative LODs), it also becomes one of the most sensitive elemental analytical techniques (Harris, 2010).

Chapter 2

Experimental

In this chapter all experimental work in this study will be shown, which was an arranged as sampling, instrumental measurements, preparation of solutions, chemicals of analytical reagents grade purity and deionized water were used. All glass wares were washed with sulfochromic acid rising with detergent and rinsed with double distilled water before drying in the oven

2.1. Chemicals and Reagents

All reagents were of analytical grade. Deionized water was used throughout the study. Glassware and sampling bottles cleaned by soaking in 10% (v/v) nitric acid and rinsed with deionised water and dried prior using.

All standard reagent solution were stored in polyethylene bottles.

- 1000mg/l Pb stock standard solution.
- 1000mg/l Cd stock standard solution.
- 1000mg/l Cr stock standard solution.
- Nitric acid concentration (65% HNO_3) RIEDEL-DE HAËN AG.
- 1M HNO_3 :It was prepared by dissolving 6.92 ml nitric acid conc. in 100ml deionized water.
- Hydrogen peroxide (30%) were purchased from Merck India Ltd.

2.2. Apparatus and Equipments

- Analytical balance.
- Drying oven.
- Hotplate.

2.3. Instrumentation

2.3.1. The X-ray fluorescence (XRF)

S2 RANGER is energy-dispersive X-ray fluorescence (EDXRF) spectrometer was used for the determination of Pb, Cd and Cr in paint samples.

2.3.2. Graphite furnace atomic absorption spectrophotometer (GFAAS)

A Shimadzu model AA-6800 Series atomic absorption spectrophotometer (GFAAS) was used for the determination of Pb, Cd and Cr level in pigments samples.

2.4. Sampling

2.4.1. Paint Samples

Thirty of white oil based paint samples were collected from five different companies with two different serial numbers for each company in Benghazi city. The collection, description, and handling terminology of paint chips are in accordance with American Society of Testing Materials (ASTM) Designation E 1610-95, Standard Guide for Forensic Paint Analysis and Comparison (U.S.EPA,2001).

In the table (2.1), codes were given to the five paint companies, which are A,B,C,D,E. Each of the companies has two different serial numbers, with sub symbols

(a,b).

Table (2.1): Codes of the companies and their serial numbers used in the this work for oil paints.

Company	***Different Serial Numbers***
A	**A_a , A_b**
B	**B_a , B_b**
C	**C_a ,C_b**
D	**D_a , D_b**
E	**E_a , E_b**

The cans of paint containing liquid paint were shaken for 20 min. After waiting 5 min after shaking, each wet paint samples were applied onto individual clean glass slides (10cm×10cm.) using different glass rods for each sample to avoid any cross contamination. Samples, thus applied were left to dry for a minimum of 72 hours, after drying samples were scraped off from glass slides using sharp and clean knives and then collected in polyethylene container and stored at room temperature.

paint samples were taken on a glass slide and placed in an oven at 120°C for 2 hours to remove any moisture.

2.4.1.1. Preparing Samples for XRF Analysis

The sample preparation for XRF analysis under taken was a pressed pellet technique, the mixture milled for the size reduction of hard and brittle sample materials for subsequent XRF analysis is the Vibratory Disc Mill and then pressed at high pressure. Inside the grinding jar the grinding tools, usually a ring, are moved in such a way that the sample is crushed by impact and friction effects. With this size reduction principle the required reproducible analytical fineness is achieved after very short grinding times.

XRF applications pellets with a plane surface are used. In contrast to lose powder, a pellet has the advantage that the element concentration detected by the x-ray is higher because the material is more compact (Beckhoff *et al.*, 2006).

2.4.2. *Pigments Samples*

Twelve color pigment samples manufactured by foreign companies were collected. Blue, green, red and yellow pigments were analysed according to standard operating procedures (U.S.EPA, 2001).

In the table (2.2), codes have been given according to the company and the product serial number to the four color pigment.

Table (2.2): Codes of the color pigment samples used in this work for the pigments.

Color pigment	**Code**
Blue	F_1,F_2,F_3
Green	G_1,G_2,G_3,G_4
Red	H_1,H_2,H_3,H_4
Yellow	I_1,I_2,I_3,I_4

Pigment samples were applied onto individual clean glass slides (5cm× 5cm) and dried at 80°C in an oven for 6hr After drying, samples were scraped off from the glass surfaces using sharp and clean knives. One knife per sample was used to avoid any contamination.

Thus scraped samples were collected in polyethylene container. After drying samples were scraped off from glass slides using sharp knife and collection of polyethylene container were stored at room temperature.

2.4.2.1. Digestion method of pigments samples for GFAAS analysis

0.1gr of each of the dried pigment sample was weighed accurately and transferred into 100 ml beaker, and then 3.0 ml of concentrated HNO_3 and 1.0 ml of H_2O_2 were added and covered with watch glass.

Reagent blank was also taken. Samples and reagent blank were then heated on a hot plate at 140^oC until most of the acid was evaporated. These were then removed from hot plate and allowed to cool at room temperature. 2 ml of HNO_3 and 1.0 ml 30% H_2O_2 were added into the beakers and dried on hot plate to dryness and then allowed to cool. This step was repeated once again. Watch glass and walls of beaker were rinsed with 5.0 ml of 1M HNO_3. Solution was evaporated gently to dryness on the hot plate and then cooled. 1.0 ml of concentrated HNO_3 was added to residue and samples were then swirled for a minute or so to dissolve soluble species (U.S.EPA, 2001).

Then rinse down the side of the beaker and filtered the sample using filter paper 41 Ashless (Whatman) into 100ml volumetric flask and diluted to the mark with deionized water mixed vigorously.

2.5. Operating condition and opimization

2.5.1. Measurement parameters for EDXRF

Measurements were performed on an S2 RANGER with XFlash® detector, in vacuum with a 30 mm sample holder mask. The measurement conditions given in table (2.3) were used.

In order to achieve the best measurement statistics, a counting time of 200 s and fixed current of 130 µA were used. The overall processing time per sample (including sample handling, evacuating the sample chamber and actual counting time for the measurement) was 6 minutes

Table (2.3): Measurement conditions parameters for EDXRF

Voltage [kV]	**Current [μA]**	**Beam Filter**	**Live Time [s]**
20	130	None	200

2.5.2. Measurement parameters for GFAAS

The optimum GFAAS operating condition used for quantitative measurements for Pb, Cd and Cr are listed in table (2.4).

Table (2.4): GFAAS operating condition used for quantitative measurements.

	Pb	**Cd**	**Cr**
Wave Length (nm)	283.3	228.8	357.9
Slit Width (nm)	1.0	1.0	0.5
Lamp Current Law (MA)	12	8	10
Sample volume (μL)	20	20	20
Drying step (ºC)	250	250	150
Ashing step (ºC)	800	500	800
Atomization step (ºC)	2400	2200	2300
Cleaning step (ºC)	2500	2400	2500

2.6. Preparation of standard curve for GFAAS

Standard solutions were prepared to obtain working solutions used to obtain the calibration curves, lower concentration standards were prepared daily from their stock standard solutions. The preparations were as follows.

2.6.1. Standard Curve of Lead.

Concentrations of 0.00, 1.00, 5.00, 10.00 μg/kg (ppb) of Pb were prepared from 100ppb solution, which was prepared from serial dilutions of a 1000 mg/L stock standard.

Table (2.5): The measured absorbance of lead working standard solution at 25^{o}C (n=3) using graphite atomic absorption spectrometry.

Concentration ppb	**Absorption**	**±SD**
0.00	0.0066	0.000990
1.00	0.0259	0.001980
5.00	0.1270	0.008415
10.00	0.2314	0.015344

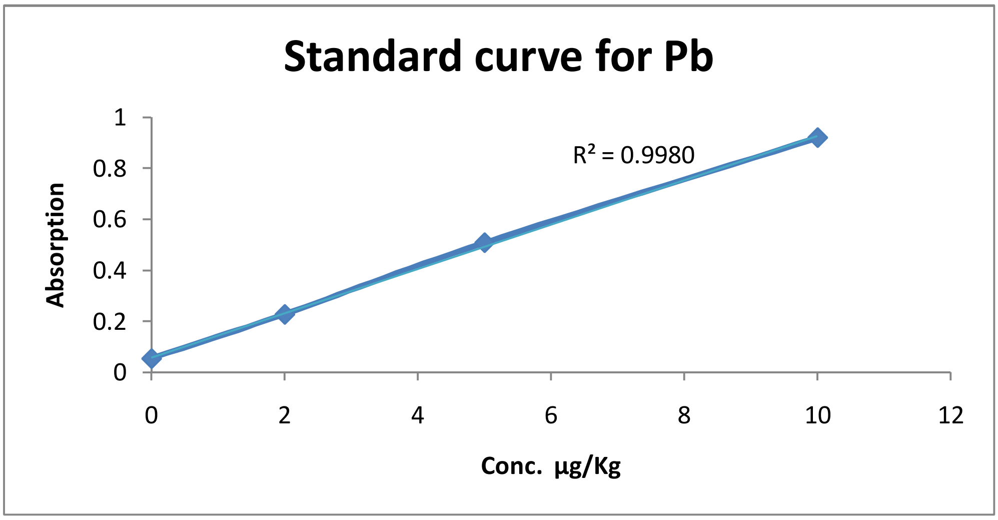

Figure (2.1): Calibration curve for lead obtained by using GFAAS

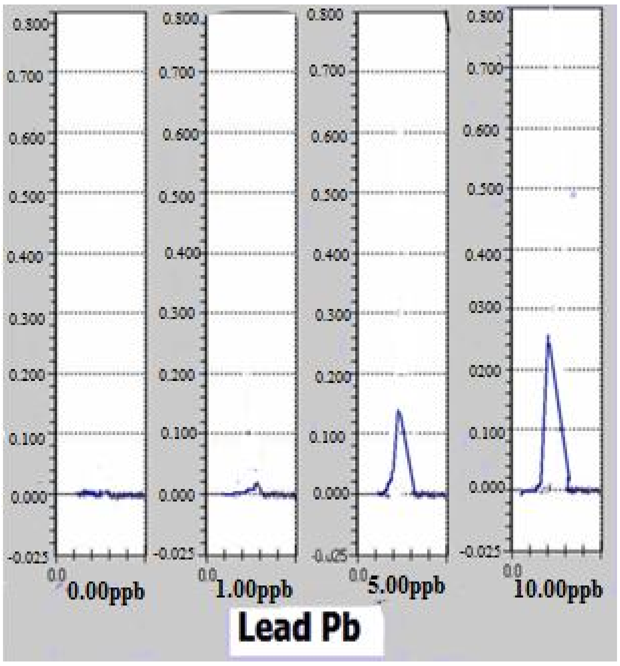

Figure (2.2): Calibration standard profiles for lead obtained by using GFAAS

2.6.2. Standard Curve of Cadmium.

Standards of 0.00, 1.00, 3.00, 5.00 µg/kg (ppb) of Cd were prepared by dilution of 10ppb solution.

Table (2.6): The measured absorbance of cadmium working standard solution at 25°C (n=3) using graphite atomic absorption spectrometry.

Concentration ppb	**Absorption**	**±SD**
0.00	0.0032	0.001909
1.00	0.2396	0.018102
3.00	0.6321	0.027365
5.00	1.0034	0.000283

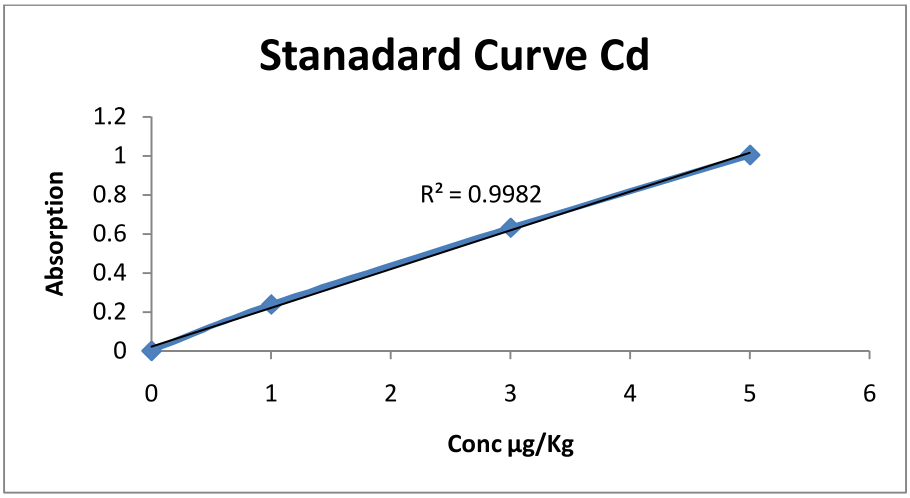

Figure (2.3): Calibration curve obtained by using GFAAS.

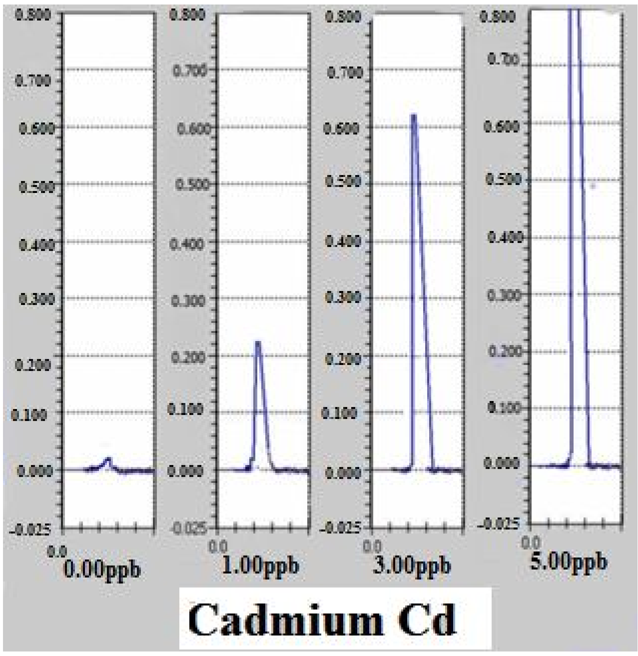

Figure (2.4): Calibration standard profiles for cadmium obtained by using GFAAS

2.6.3. Standard Curve of Chromium.

Concentrations of 0.00, 2.00, 5.00, 10.00 µg/kg (ppb) of Cr were prepared by dilution of 100 ppb solution.

Table (2.7): The measured absorbance of chromium working standard solution at 25°C (n = 3) using graphite atomic absorption spectrometry:

Concentration ppb	Absorption	±SD
0.00	0.0547	0.032527
2.00	0.2280	0.007990
5.00	0.5084	0.002192
10.00	0.9202	0.025385

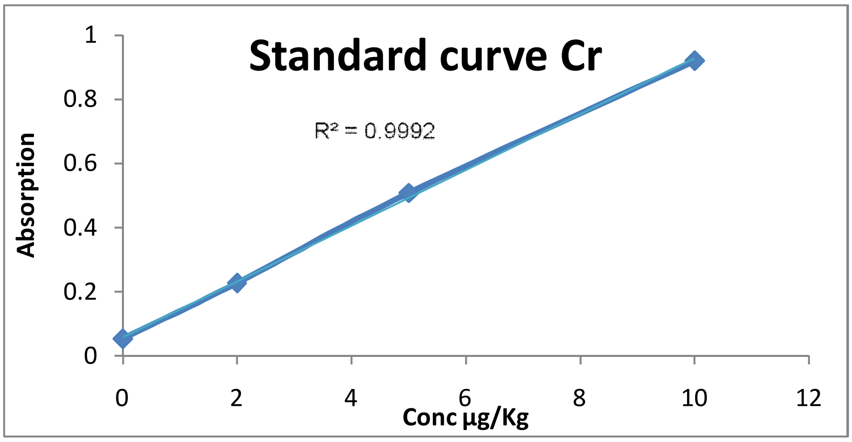

Figure (2.5): Calibration curve for chromium obtained by using GFAAS

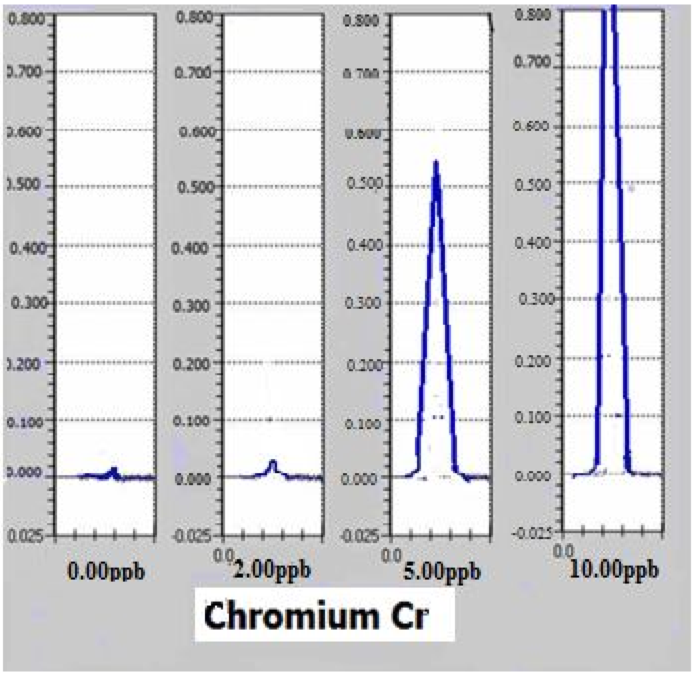

Figure (2.6): Calibration standard profiles for chromium obtained by using GFAAS.

Chapter 3

Results and Discussion

In this chapter all results and their discussion of our study will be shown. The results obtained for the analyses of some heavy metal (lead, cadmium and chromium) in the white oil-based paint samples using the energy dispersion x-ray fluorescence spectrometer (EDXRF) from different paint companies.

Each of the companies chosen has different serial numbers, this different is according to the date of mixed the paints components and offers on the market.

Addition to the color pigment ingredient samples (blue, green, red and yellow) using furnace graphite atomic absorption spectrometry, collected from the products of the European company, were also analyzed.

3.1. White oil-based paints

3.1.1. Determination of lead using EDXRF

Result of the lead analysis for white oil based paint samples taken from difference companies shown in the tables:

Table (3.1): The average concentration of lead in white oil paint samples of the company A (n=6) using EDXRF.

	Pb %	**Std. Deviation**	**±SEM**	**mg/Kg**
$A_{a\,1}$	0.0518	0.00117	0.00048	518
$A_{a\,2}$	0.0517	0.00103	0.00042	517
$A_{a\,3}$	0.0520	0.00089	0.00037	520
$A_{b\,1}$	0.0302	0.00117	0.00048	302
$A_{b\,2}$	0.0302	0.00194	0.00079	302
$A_{b\,3}$	0.0295	0.00164	0.00067	295

In the table (3.1) we found the company A has a different range of lead concentration and percentage between the two different serial numbers. In A_a we found that the range of lead concentration is 517 mg/kg – 520 mg/kg, lead percentage is 0.0517% - 0.0520%. In addition, for A_b 295 mg/kg- 302 mg/kg, lead percentage is 0.0295% -0.0302 %. These values of lead concentration indicate that company A is not depended on Libyan standard specification of paint (0.06%), which based on the ASTM specification for paint and the Consumer Product Safety Commission limited the lead in residential paint to 0.06 percent (600 ppm by dry weight). In addition, the differences in the range of lead concentration and percentage between the two different serial numbers, which showed in table (3.1), indicate that the company A has no quality control on its products.

Table (3.2): The average concentration of lead in white oil paint samples of the company B (n=6) using EDXRF.

	Pb %	**Std. Deviation**	**±SEM**	**mg/Kg**
$\mathbf{B_{a\,1}}$	0.0405	0.00187	0.00076	405
$\mathbf{B_{a\,2}}$	0.0402	0.00172	0.00070	402
$\mathbf{B_{a\,3}}$	0.0397	0.00216	0.00088	397
$\mathbf{B_{b\,1}}$	0.0497	0.00163	0.00067	497
$\mathbf{B_{b\,2}}$	0.0505	0.00138	0.00056	505
$\mathbf{B_{b\,3}}$	0.0502	0.00117	0.00048	502

Table (3.2) shows the results of company B. No high difference in lead concentration and lead percentage for the two different serial numbers was found.

For the serial number B_a, the lead concentration and percentage obtained from our measurements are in the range (397mg/Kg - 405mg/Kg, 0.0397% - 0.0405%) respectively. B_b has a lead concentration in the range 497mg/Kg - 505mg/Kg and percentage is 0.0497% - 0.0505%. The results, shown in table (3.2), indicate no difference between the concentration in the two serial numbers, that mean the company B has a quality control.

Table (3.3): The average concentration of lead in white oil paint samples of the company C (n=6) using EDXRF.

	Pb %	**Std. Deviation**	**±SEM**	**mg/Kg**
$C_{a\,1}$	0.0290	0.00110	0.00045	290
$C_{a\,2}$	0.0295	0.00217	0.00089	295
$C_{a\,3}$	0.0292	0.00194	0.00079	292
$C_{b\,1}$	0.0303	0.00121	0.00049	303
$C_{b\,2}$	0.0300	0.00219	0.00089	300
$C_{b\,3}$	0.0298	0.00117	0.00048	298

Table (3.3) shows the results for the company C, we found that has approximately the same lead concentration in two different serial numbers. C_a has lead concentration in the range 290 mg/Kg - 295 mg/Kg and percentage is 0.0290% - 0.0295% and C_b has a lead concentration is 298 mg/Kg - 303 mg/Kg, 0.0298% - 0.0303% respectively. From these values of the lead concentration and percentage. There is no difference in the lead concentration and percentage between the two difference serial numbers, it means that, company C has a quality control in its products.

Table (3.4): The average concentration of lead in white oil paint samples of the company D (n=6) using EDXRF.

	Pb %	**Std. Deviation**	**±SEM**	**mg/Kg**
$D_{a\,1}$	0.0500	0.00290	0.00118	500
$D_{a\,2}$	0.0493	0.00225	0.00092	493
$D_{a\,3}$	0.0500	0.00237	0.00097	500
$D_{b\,1}$	0.0605	0.00187	0.00076	605
$D_{b\,2}$	0.0593	0.00163	0.00067	593
$D_{b\,3}$	0.0602	0.00279	0.00114	602

In the company D, we found that, this company has approximately the same concentration in two different serial numbers table (3.4).

For D_a the lead concentration and percentage obtained from our measurements are in the range 493 mg/Kg – 500 mg/Kg, 0.0493% - 0.050%, and for the serial number D_b has a lead concentration and percentage in the range 593 mg/Kg - 605 mg/Kg, 0.0593% - 0.0605%. from these values of the lead concentration and percentage we found there is no different in the lead concentration and percentage between the two different serial numbers, that is mean, company D has a quality control.

Table (3.5): The average concentration of lead in white oil paint samples of the company E (n=6) using EDXRF.

	Pb %	**Std. Deviation**	**±SEM**	**mg/Kg**
$E_{a\,1}$	0.0283	0.00175	0.00071	283
$E_{a\,2}$	0.0298	0.00147	0.00060	298
$E_{a\,3}$	0.0295	0.00187	0.00076	295
$E_{b\,1}$	0.0992	0.00376	0.00154	992
$E_{b\,2}$	0.1002	0.00417	0.00170	1002
$E_{b\,3}$	0.1002	0.00542	0.00221	1002

The company E has different range of lead concentration and percentage in the two different serial numbers.

In the serial number E_a the lead concentration and percentage obtained from our measurements are the range 283 mg/Kg – 298 mg/Kg, 0.0283% - 0.0298%, and for the serial number E_b has a lead concentration and percentage in the range 992 mg/Kg - 1002 mg/Kg, 0.0992% - 0.1002%.

In the serial number E_a we found that has lower concentration than the serial number E_b. That mean, no quality control on the lead concentration between the two different serial numbers of company E.

E_a is limit the permissible level in paint but E_b is the highest the maximum limit of lead concentration, indicate that no quality control in this company.

The results of the total concentrations of lead (Pb) in white oil- based paint samples showed that all of them still contained lead with relatively high levels in a few instances are given in table (3.6) and figure (3.1).

Table (3.6): The average of lead concentration and percentage in each serial number of each company, in our samples using EDXRF, n=6 where n= the number of samples of each serial number.

Company	**Pb %**	**mg/Kg**
A_a	0.0518	518
A_b	0.0299	299
B_a	0.0401	401
B_b	0.0501	501
C_a	0.0292	292
C_b	0.0301	301
D_a	0.0498	498
D_b	0.0600	600
E_a	0.0292	292
E_b	0.0998	998

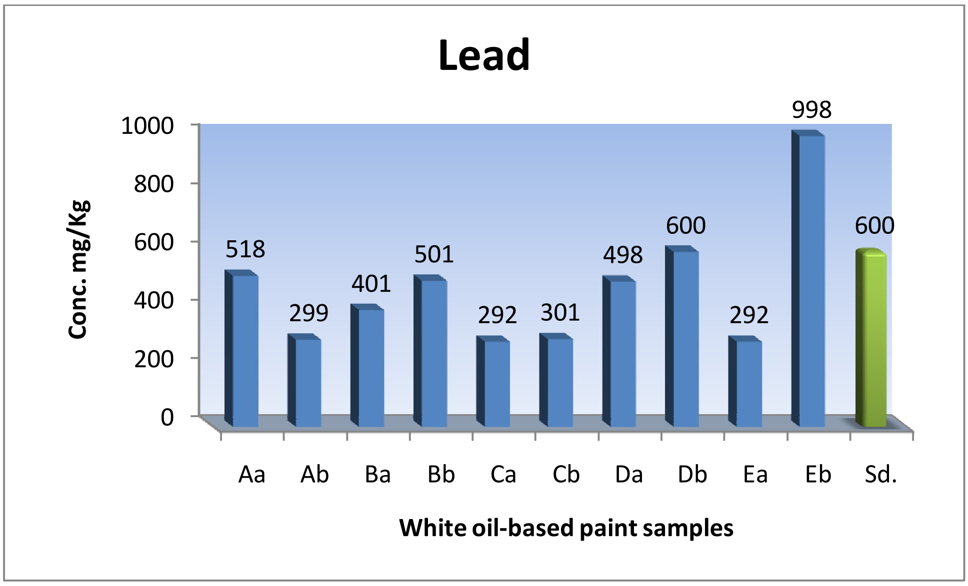

Figure (3.1): Lead concentration in each serial number of each company

From tables (3.6) and figure (3.1) there are differences between the companies in lead concentration and percentage. In addition, there is a different in the two difference serial numbers for each company, especially in a sample E.

The A company has a different lead concentration and percentage between the two serial numbers A_a and A_b, where A_a= 0.0518% and A_b = 0.0299%. This indicates that has no quality control on the A company and its product.

the company C has not been different between the two different serial numbers which we did our measuring, C_a=0.0292%, C_b= 0.0301%). We found that is the companies which have the low values in lead concentration and percentage in paint samples. This means, which is the company with lower toxic lead in paint.

The companies B and D have not been high different between the two different serial numbers which we did our measuring, B (B_a= 0.0401%, B_b= 0.0501%), and for D company (D_a = 0.0498% and D_b= 0.0600%, which indicates this company have not a quality control in its products.

However, the company E has been high different between the two different serial numbers E_a = 0.0292% and E_b = 0.0998%. Which indicate this company has not a quality control on its product.

The level of lead in paint samples in this study was compared with other results by other studies in different countries, the average value of lead obtained from samples of paints in the South African was paint lead concentration larger than 5000 mg/Kg (Montgomery and Mathee, 2005), and paint samples obtained from China, India and Malaysia 66% of new paint samples were found to contain 5000 ppm (0.5%) or more of lead (Clark *et al*., 2006).

The average value of lead in the paint in Nigeria was 14500ppm were found that 96%of the paints had been higher than recommended levels of lead (Adebamowo, 2007).

A study on lead in paints in India conducted by Toxics Link lead content was found to be high up to 140,000 ppm in many oil-based enamel paints (Kumar, 2007).

When our results were compared with these values we found that they are lower than those results obtained from our study, but the average values of lead in Saudi Arabian was less than 0.5% (AL Eshaikh and Kadachi, 2007).

In Bangladesh, the range of lead paint samples ranged from 55 to 114010 ppm in enamel paint (Hossain *et al.*, 2013).

When our results were compared with the maximum recommended limit by in Libya standard specification of paint of 0.06%, which based on the ASTM specification for paint and the Consumer Product Safety Commission limited the lead in residential paint to 0.06 percent (600 ppm by dry weight) (CPSC, 1977), and the Chinese Standards (Pb ≤ 0.009% or 90 ppm) (Barboza, 2007).

We noted lead levels in white oil-based paint less than or equal to 0.06% by weight except E company was 0.0998% higher than 0.06%, but they were higher than Chinese Standards (Pb ≤ 0.009% or 90 ppm)

3.1.2. Determination of Cadmium using EDXRF

Result of the cadmium analysis for white oil based paint samples taken from different companies shown in the tables:

Table (3.7): The average concentration of cadmium in white oil paint samples of the company A (n=6) using EDXRF.

	Cd %	**Std. Deviation**	**±SEM**	**mg/Kg**
$A_{a\,1}$	0.0037	0.00197	0.00080	37
$A_{a\,2}$	0.0040	0.00228	0.00093	40
$A_{a\,3}$	0.0035	0.00243	0.00099	35
$A_{b\,1}$	0.0028	0.00075	0.00031	28
$A_{b\,2}$	0.0028	0.00075	0.00031	28
$A_{b\,3}$	0.0028	0.00075	0.00031	28

In the company A, cadmium with different concentration and percentage in the two different serial numbers (table 3.7).

In the serial number A_a, we found that has a higher concentration of cadmium than other samples of two serial number. A_a has cadmium concentration between (35 mg/Kg - 40 mg/Kg) and A_b has is 28 mg/Kg. That is mean, no quality control on cadmium concentration.

Table (3.8): The average concentration of cadmium in white oil paint samples of the company B (n=6) using EDXRF.

	Cd %	**Std. Deviation**	**±SEM**	**mg/Kg**
$B_{a\,1}$	0.0003	0.00052	0.00021	3
$B_{a\,2}$	0.0003	0.00052	0.00021	3
$B_{a\,3}$	0.0003	0.00052	0.00021	3
$B_{b\,1}$	0.0005	0.00055	0.00022	5
$B_{b\,2}$	0.0005	0.00055	0.00022	5
$B_{b\,3}$	0.0005	0.00055	0.00022	5

In the company B, we found in table (3.8) that cadmium has approximately the same concentration and percentage in the two different serial numbers. For the serial number a , b we found that has a cadmium concentration in the range 3 mg/Kg – 5 mg/Kg, this less toxic in difference of cadmium percentage between the two serial number. That is mean, company B has a quality control on its products.

Table (3.9): The average concentration of cadmium in white oil paint samples of the company C (n=6) using EDXRF.

	Cd %	Std. Deviation	±SEM	mg/Kg
$C_{a\,1}$	0.0013	0.00052	0.00021	13
$C_{a\,2}$	0.0010	0.00063	0.00026	10
$C_{a\,3}$	0.0012	0.00117	0.00048	12
$C_{b\,1}$	0.0017	0.00121	0.00049	17
$C_{b\,2}$	0.0013	0.00103	0.00042	13
$C_{b\,3}$	0.0015	0.00105	0.00043	15

From the table (3.9), we found the company C has a different range of cadmium concentration and percentage in the two different serial numbers.

In C_a we found that, the range of cadmium concentration is 10 mg/Kg -13 mg/Kg, cadmium percentage is 0.0010% - 0.0013%. In addition, C_b for has cadmium 13 mg/Kg - 17 mg/Kg, cadmium percentage is 0.0013% - 0.0017%. We found on high difference of cadmium percentage between the two serial number. These values of cadmium concentration indicate that the company C is depended on standard specification of paint.

Table (3.10): The average concentration of cadmium in white oil paint samples of the company D (n=6) using EDXRF.

	Cd %	Std. Deviation	±SEM	mg/Kg
$D_{a\,1}$	0.0028	0.00075	0.00031	28
$D_{a\,2}$	0.0028	0.00075	0.00031	28
$D_{a\,3}$	0.0030	0.00089	0.00037	30
$D_{b\,1}$	0.0028	0.00075	0.00031	28
$D_{b\,2}$	0.0028	0.00075	0.00031	28
$D_{b\,3}$	0.0027	0.00052	0.00021	27

The table (3.10) showed the result for company D. Cadmium concentration were approximately the same in two different serial numbers. D_a has a cadmium concentration in the range (28 mg/Kg - 30 mg/Kg), and D_b has a cadmium concentration in the range (27 mg/Kg - 28 mg/Kg). We found there is no difference in the cadmium concentration and percentage between the two different serial numbers, that means, company D has a quality control in its product.

Table (3.11): The average concentration of cadmium in white oil paint samples of the company E (n=6) using EDXRF.

	Cd %	**Std. Deviation**	**±SEM**	**mg/Kg**
$E_{a\,1}$	0.0017	0.00082	0.00033	17
$E_{a\,2}$	0.0017	0.00082	0.00033	17
$E_{a\,3}$	0.0017	0.00082	0.00033	17
$E_{b\,1}$	0.0028	0.00075	0.00031	28
$E_{b\,2}$	0.0030	0.00089	0.00037	30
$E_{b\,3}$	0.0028	0.00075	0.00031	28

From our result obtained from the measurements of cadmium concentration in the company E, which showed above the table (3.11), we found that company has cadmium concentration in products with different concentration in the two different serial numbers. For serial number E_a we found that has a cadmium concentration is 17 mg/Kg, for the serial number E_b the cadmium concentration is in the range 28 mg/Kg - 30 mg/Kg, this difference in the cadmium concentration and percentage between the two different serial numbers in the company E, which indicates no quality control on its products.

Table (3.12): The average of cadmium concentration and percentage in each serial number of each company, in our samples using EDXRF, n=6 where n= the number of samples of each serial number.

company	**Cd %**	**mg/Kg**
A_a	0.0038	38
A_b	0.0028	28
B_a	0.0003	3
B_b	0.0005	5
C_a	0.0015	15
C_b	0.0012	12
D_a	0.0028	28
D_b	0.0029	29
E_a	0.0017	17
E_b	0.0029	29

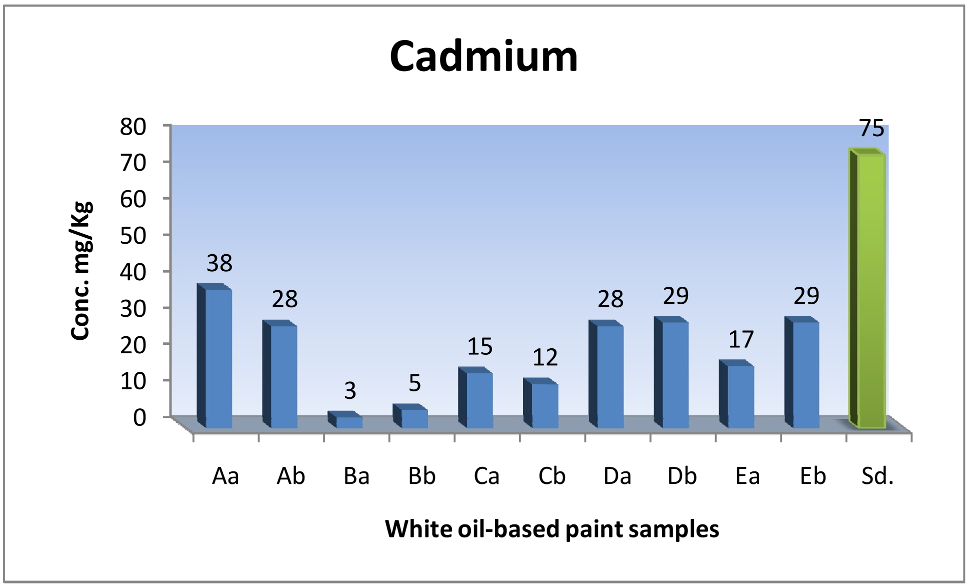

Figure (3.2): Cadmium concentration in each serial number of each company.

From the table (3.12) and figure(3.2), we found there are no high difference between the companies (product) in cadmium concentration and percentage. But there is a different in the two different serial numbers in the company A and E.

A and E companies have the high different between cadmium concentration in the two different serial number, which we did our measuring A(A_a , A_b had 38 mg/Kg – 28 mg/Kg respectively), and for E company E_a = 17 mg/Kg , E_b = 29 mg/Kg. That mean had no a quality control on them products.

The companies B and D have approximately the same cadmium concentration in two different serial numbers. we found of the company B has the low value in cadmium concentration (B_a=3mg/Kg , B_b=5mg/Kg) this means, which is the company with less toxic cadmium in paint. But the company D has not been different in the cadmium concentration between the two different serial numbers D_a and D_b, where D_a = 28mg/Kg and D_b = 29mg/Kg. That indicates these companies have a quality control on them the product.

While the company C has no high difference between the two different serial numbers C_a = 15 mg/Kg and C_b = 12 mg/Kg. This means that, company C has a quality control.

When our results were compared with the maximum recommended limit by the ASTM specification for paint and the Chinese Standards limited the cadmium in residential paint to (Cd≤ 75 ppm) (CPSIA. 2008). We noted cadmium levels in white oil-based paint in all companies less than 75 ppm.

3.1.3. Determination of Chromium using EDXRF.

Result of the chromium analysis for white oil based paint samples taken from different companies shown in the following tables:

Table (3.13): The average concentration of chromium in white oil paint samples of the company A (n=6) using EDXRF.

	Cr %	**Std. Deviation**	**±SEM**	**mg/Kg**
$A_{a\,1}$	0.0030	0.00126	0.00052	30
$A_{a\,2}$	0.0030	0.00089	0.00037	30
$A_{a\,3}$	0.0028	0.00117	0.00048	28
$A_{b\,1}$	0.0060	0.00141	0.00058	60
$A_{b\,2}$	0.0060	0.00141	0.00058	60
$A_{b\,3}$	0.0062	0.00147	0.00060	62

In the company A, we found that chromium has different concentration and percentage in the two different serial numbers (table 3.13).

In the serial number (A_b) we found that has a higher concentration of chromium than the serial number A_a. That is mean, no quality control on chromium concentration of the company A, for the serial number (A_a) the chromium concentration and percentage obtained from our measurement are in the range (28mg/Kg - 30mg/Kg) respectively. A_b has the range of chromium concentration is (60 mg/Kg- 62 mg/Kg).

Table (3.14): The average concentration of chromium in white oil paint samples of the company B (n=6) using EDXRF.

	Cr %	**Std. Deviation**	**±SEM**	**mg/Kg**
$B_{a\,1}$	0.0013	0.00052	0.00021	13
$B_{a\,2}$	0.0012	0.00041	0.00058	12
$B_{a\,3}$	0.0013	0.00052	0.00021	13
$B_{b\,1}$	0.0005	0.00055	0.00022	05
$B_{b\,2}$	0.0003	0.00052	0.00021	03
$B_{b\,3}$	0.0003	0.00052	0.00021	03

From the table (3.14) which showed the results for our measurements of the company B, we found that has a chromium in its products, and approximately the same chromium concentration in two different serial numbers, B_a has a chromium concentration. In the range (12mg/Kg - 13mg/Kg). B_b has chromium concentration the range (3mg/Kg - 5mg/Kg), we found that, there is no difference in chromium concentration and percentage between the two different serial numbers. It means that, in this company B has a quality control in its products.

Table (3.15): The average concentration of chromium in white oil paint samples of the company C (n=6) using EDXRF.

	Cr %	**Std. Deviation**	**±SEM**	**mg/Kg**
$C_{a\,1}$	0.0007	0.00082	0.00033	7
$C_{a\,2}$	0.0005	0.00084	0.00034	5
$C_{a\,3}$	0.0005	0.00084	0.00034	5
$C_{b\,1}$	0.0008	0.00075	0.00031	8
$C_{b\,2}$	0.0010	0.00063	0.00026	10
$C_{b\,3}$	0.0010	0.00063	0.00026	10

In the company C showed a lower chromium in oil-based paint samples in two different serial number. We found that has a chromium concentration in two serial numbers (a,b) in the company C, in the range (5mg/Kg – 10mg/Kg), and has chromium percentage in the range(0.0005% - 0.0010%. It means that, company has a quality control in its product.

Table (3.16): The average concentration of chromium in white oil paint samples of the company D (n=6) using EDXRF.

	Cr %	**Std. Deviation**	**±SEM**	**mg/Kg**
$D_{a\,1}$	0.0022	0.00075	0.00031	22
$D_{a\,2}$	0.0023	0.00103	0.00042	23
$D_{a\,3}$	0.0017	0.00042	0.00049	17
$D_{b\,1}$	0.0022	0.00075	0.00031	22
$D_{b\,2}$	0.0025	0.00055	0.00022	25
$D_{b\,3}$	0.0022	0.00075	0.00031	22

Table (3.16) shows the results for company D, we found that has a chromium in its products and approximately the same chromium concentration in two difference serial numbers. D_a has a chromium concentration in the range (17 mg/Kg - 23 mg/Kg). D_b has a chromium concentration in the range (22 mg/Kg - 25 mg/Kg). From these values of the chromium concentration and percentage we found that, there is no difference in the chromium concentration and percentage between the two different serial numbers. It means that, company D has a quality control company which has the higher chromium concentration the other companies, which measured in our study.

In company E, the chromium concentration and percentage between the two different serial numbers (a,b) were none.

Table (3.17): The result of chromium conc. and percentage in each serial number of each company, in our samples using EDXRF, n=6 where n=the number of samples of each serial number

Company	Cr %	mg/Kg
A_a	0.0029	29
A_b	0.0061	61
B_a	0.0013	13
B_b	0.0004	04
C_a	0.0021	21
C_b	0.0023	23
D_a	0.0058	58
D_b	0.0029	29
E_a	0.0000	000
E_b	0.0000	000

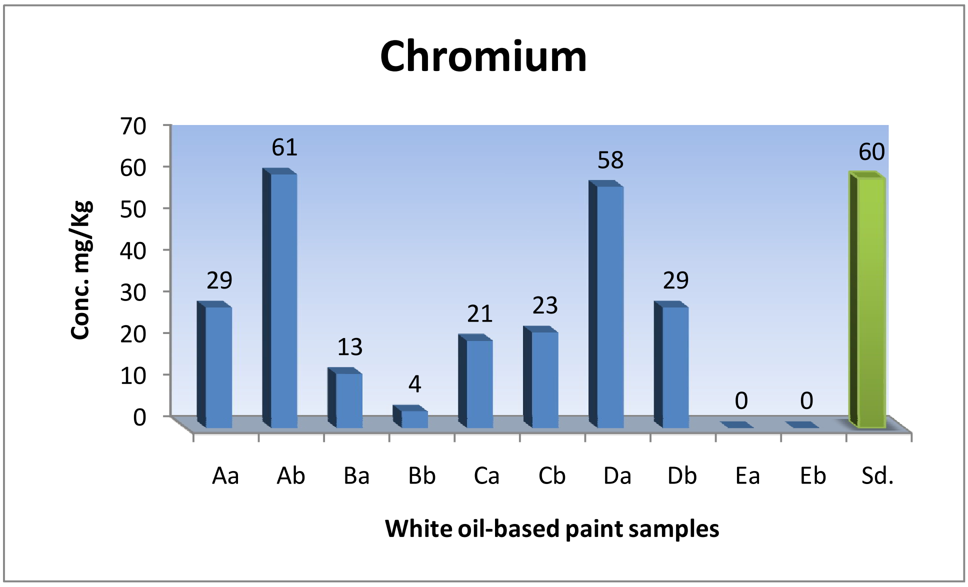

Figure (3.3): Chromium concentration in each serial number of each company.

From the table (3.17) and figure(3.3) showed undetected chromium conc. in the company E, while in another we found that is not high different between the companies (product) in cadmium conc. and percentage.

In the company A has a different chromium concentration between serial numbers (A_a = 29 mg/Kg and A_b = 61mg/Kg), this indicates that has no a quality control.

We found the companies B and D have not high different between the two serial numbers a, b (B_a =13mg/Kg , B_b=4mg/Kg) and (D_a= 58mg/Kg , D_b = 29mg/Kg). Which indicates that these companies have a quality control on them products.

The company C has not high different between the two serial numbers (C_a , C_b have 21mg/Kg and 23mg/Kg, respectively). This mean, which is the company with less chromium conc. in paint.

When our results were compared with the maximum recommended limit by the ASTM specification for paint and the Chinese Standards limited the chromium in residential paint to ($Cr \leq 60$ ppm)(CPSIA, 2008). We noted chromium levels in white oil-based paint in all companies less than equal 60 ppm.

3.2. Determination of trace metal in the color pigments

The results for the color pigment samples were analyzed for lead, cadmium and chromium are shown in table (3.18) and figure (3.4).

Table (3.18): The average concentrations in mg/kg (ppm) of each of the elements detected in the color pigment ingredient samples (blue, green, red and yellow) using furnace graphite atomic absorption spectrometry.

Symbols		Lead			Cadmium			Chromium		
		µg/Kg	***mg/Kg***	***%***	***µg/Kg***	***mg/Kg***	***%***	***µg/Kg***	***mg/Kg***	***%***
F	**F1**	85.10	0.08510	0.0085	13.82	0.01382	0.00138	32.85	0.03285	0.00329
	F2	86.50	0.08650	0.0087	13.95	0.01395	0.00140	32.46	0.03246	0.00325
	F3	86.58	0.08658	0.0087	13.86	0.01386	0.00140	32.61	0.03261	0.00326
G	**G1**	52.34	0.05234	0.0052	11.57	0.01157	0.00116	41.75	0.04175	0.00418
	G2	54.10	0.05410	0.0054	11.83	0.01183	0.00118	41.52	0.04152	0.00416
	G3	53.90	0.05390	0.0054	11.74	0.01174	0.00117	41.38	0.04138	0.00414
H	**H1**	77.90	0.07790	0.0078	29.73	0.02973	0.00297	1.52	0.00152	0.00015
	H2	77.52	0.07752	0.0077	29.65	0.02965	0.00297	1.56	0.00156	0.00016
	H3	77.86	0.07786	0.0078	29.43	0.02943	0.00294	1.53	0.00153	0.00015
I	**I1**	46.62	0.04662	0.0047	1.83	0.00183	0.00018	2.82	0.00282	0.00028
	I2	43.65	0.04365	0.0044	1.84	0.00184	0.00018	2.79	0.00279	0.00028
	I3	45.51	0.04551	0.0045	1.86	0.00186	0.00019	2.84	0.00284	0.00028

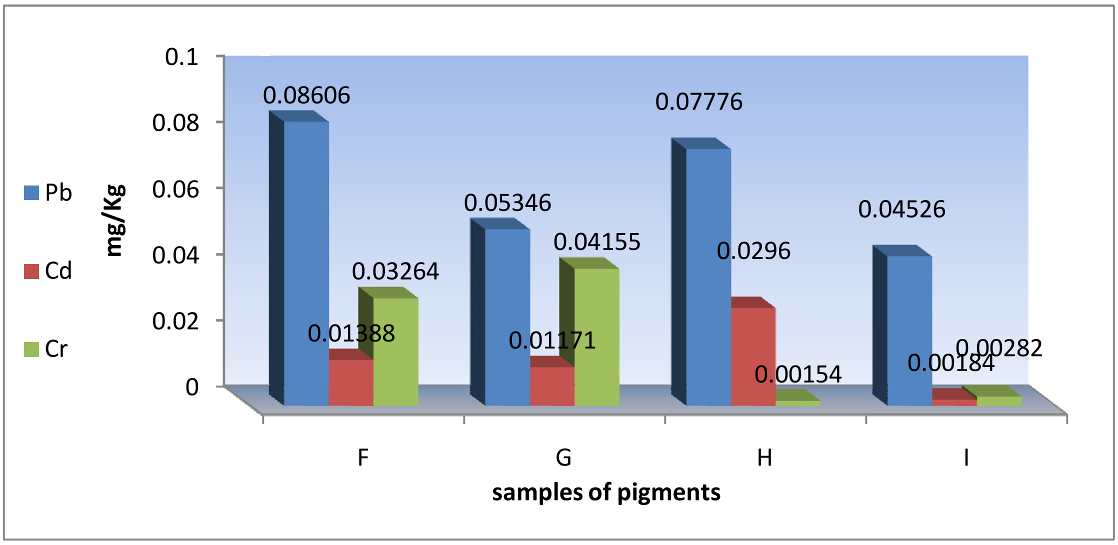

Figure (3.4): The average concentrations in mg/kg (ppm) of each of the elements detected in the color pigment ingredient samples.

Table (3.18) above shows the concentration levels of trace elements (Pb, Cd and Cr) in the color pigment samples we found all the color pigment samples had in the recommended level.

The average concentration of lead in all the color pigment samples ranged from 0.04365 ppm to 0.08658 ppm. The highest concentration of lead (0.08658 ppm) was detected in blue pigments. The lead concentration in different colours of pigment in decreasing was as follows:

(I>G>H>F) which yellow>red>green> blue.

The lead was detected in all pigments lower than the recommended level 600 ppm (0.06%) in the product.

The average concentration of Cadmium in all the color pigment samples between (0.02973 ppm – 0.00183 ppm), the high concentration in red pigment sample.

Cadmium levels was detected in all pigments lower than75 ppm in the product.

The chromium also ranged 0.00152 ppm to 0.04175 ppm, the high conc. in green pigment sample, we note chromium level was detection in all pigments lower than the recommended level 60ppm in the product.

Chapter 4

Conclusion

In this study, white oil paint samples were collected from five different companies in Benghazi to measure some trace elements (lead, cadmium and chromium) because of their importance as indicator of environmental pollution. Also, these three elements were estimated in paint pigments (blue, yellow, red and green) from foreign companies.

Different analytical techniques have been used to perform the elemental analysis. For white oil paint sample Energy Dispersive X-ray Fluorescence (EDXRF) has been used and Graphite Furnace Atomic Absorption Spectrometer (GFAAS) for pigments.

We found different concentrations of the three elements (Pb, Cd and Cr) in white oil paints samples among the five companies. These variations were found through paint cans' serial numbers as well as their batch numbers. For example, Lead (Pb) concentrations were higher than Chinese Standards ($Pb \leq 0.009\%$ or 90 ppm), but they were compatible with Libyan Standard Specifications ($Pb \leq 0.06\%$ or 600 ppm). For cadmium (Cd), the results were less than Chinese Standards ($Cd \leq 75$ ppm) and for chromium were also less than Chinese Standards ($Cr \leq 60$ ppm).

In addition, we found those companies have different focus on quality control for their products. For instance, companies B, C and D have no difference in lead, cadmium and chromium concentrations between two different batch numbers for each sample, which means these companies have high quality control of their products. In contrast, companies A and E, which each batch have different concentrations of the elements.

For paint pigments, all the three elements have concentrations less than the values in the white oil paints. Also,we found that the concentration of lead depends on pigment's color as follows: blue < green < red < yellow. The highest concentration of cadmium was found in sample I (yellow pigment) because it has high concentration of cadmium oxide. Sample G (green pigment) contains the highest concentration of chromium among all pigments. In general, concentration of the three elements in all pigments was less than the allowed limit of Standard Specifications.

Recommendations

1. Application of the standard Libyan paint which has been approved by international standard specifications for heavy elements to paint
2. Manufacturing paint must do analytical tests for raw materials to make sure its conform to standard specifications
3. Taken into account the process of recycling and disposal of waste in a safe manner and make every effort to minimize waste and

   emissions during the manufacturing process

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Chapter 5

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Chapter 6

Appendix

Appendix A: Statistical analysis of results obtained Using the energy dispersion X-ray fluorescence spectrometry:

Appendix section 1: Lead in white oil paint samples

Company A:

Concentration of lead in white oil paint samples(%)						
	$A_{a\,1}$	**$A_{a\,2}$**	**$A_{a\,3}$**	**$A_{b\,1}$**	**$A_{b\,2}$**	**$A_{b\,3}$**
I	0.053	0.053	0.052	0.031	0.029	0.027
II	0.052	0.050	0.052	0.032	0.033	0.029
III	0.050	0.052	0.051	0.029	0.030	0.029
VI	0.051	0.051	0.051	0.029	0.028	0.030
V	0.053	0.052	0.053	0.030	0.029	0.030
IV	0.052	0.052	0.053	0.030	0.032	0.032
Mean	**0.0518**	**0.0517**	**0.0520**	**0.0302**	**0.0302**	**0.0295**
Std. Deviation	**0.00117**	**0.00103**	**0.00089**	**0.00117**	**0.00194**	**0.00164**
±SEM	**0.00048**	**0.00042**	**0.00037**	**0.00048**	**0.00079**	**0.00067**

Company B:

Concentration of lead in white oil paint samples(%)						
	$B_{a\,1}$	**$B_{a\,2}$**	**$B_{a\,3}$**	**$B_{b\,1}$**	**$B_{b\,2}$**	**$B_{b\,3}$**
I	0.040	0.040	0.039	0.049	0.050	0.049
II	0.042	0.039	0.040	0.050	0.051	0.050
III	0.039	0.040	0.038	0.050	0.049	0.051
VI	0.043	0.038	0.041	0.052	0.053	0.052
V	0.038	0.041	0.043	0.050	0.050	0.050
IV	0.041	0.043	0.037	0.047	0.050	0.049
Mean	**0.0405**	**0.0402**	**0.0397**	**0.0497**	**0.0505**	**0.0502**
Std. Deviation	**0.00187**	**0.00172**	**0.00216**	**0.00163**	**0.00138**	**0.00117**
±SEM	**0.00076**	**0.00070**	**0.00088**	**0.00067**	**0.00056**	**0.00048**

Company C:

Concentration of lead in white oil paint samples(%)						
	$C_{a\,1}$	**$C_{a\,2}$**	**$C_{a\,3}$**	**$C_{b\,1}$**	**$C_{b\,2}$**	**$C_{b\,3}$**
I	0.029	0.028	0.029	0.032	0.027	0.031
II	0.028	0.033	0.028	0.031	0.031	0.030
III	0.031	0.031	0.031	0.031	0.033	0.029
VI	0.028	0.029	0.032	0.029	0.031	0.030
V	0.029	0.027	0.028	0.030	0.030	0.031
IV	0.029	0.029	0.027	0.029	0.028	0.028
Mean	**0.0290**	**0.0295**	**0.0292**	**0.0303**	**0.0300**	**0.0298**
Std. Deviation	**0.00110**	**0.00217**	**0.00194**	**0.00121**	**0.00219**	**0.00117**
±SEM	**0.00045**	**0.00089**	**0.00079**	**0.00049**	**0.00089**	**0.00048**

Company D:

Concentration of lead in white oil paint samples(%)						
	$D_{a\,1}$	**$D_{a\,2}$**	**$D_{a\,3}$**	**$D_{b\,1}$**	**$D_{b\,2}$**	**$D_{b\,3}$**
I	0.054	0.053	0.048	0.059	0.061	0.064
II	0.049	0.048	0.049	0.063	0.059	0.063
III	0.051	0.047	0.051	0.062	0.057	0.057
VI	0.048	0.048	0.052	0.060	0.060	0.060
V	0.052	0.051	0.053	0.061	0.061	0.059
IV	0.046	0.049	0.047	0.058	0.058	0.058
Mean	**0.0500**	**0.0493**	**0.0500**	**0.0605**	**0.0593**	**0.0602**
Std. Deviation	**0.00290**	**0.00225**	**0.00237**	**0.00187**	**0.00163**	**0.00279**
±SEM	**0.00118**	**0.00092**	**0.00097**	**0.00076**	**0.00067**	**0.00114**

Company E:

Concentration of lead in white oil paint samples(%)						
	$E_{a\,1}$	**$E_{a\,2}$**	**$E_{a\,3}$**	**$E_{b\,1}$**	**$E_{b\,2}$**	**$E_{b\,3}$**
I	0.026	0.029	0.027	0.096	0.099	0.097
II	0.031	0.031	0.029	0.103	0.096	0.096
III	0.029	0.028	0.028	0.104	0.095	0.104
VI	0.029	0.030	0.031	0.095	0.102	0.100
V	0.027	0.029	0.032	0.097	0.104	0.109
IV	0.028	0.032	0.030	0.100	0.105	0. 095
Mean	**0.0283**	**0.0298**	**0.0295**	**0.0992**	**0.1002**	**0.1002**
Std. Deviation	**0.00175**	**0.00147**	**0.00187**	**0.00376**	**0.00417**	**0.00542**
±SEM	**0.00071**	**0.00060**	**0.00067**	**0.00154**	**0.00170**	**0.00221**

Appendix section 2: Cadmium in white oil paint samples

Company A:

Concentration of cadmium in white oil paint samples(%)						
	$A_{a\,1}$	**$A_{a\,2}$**	**$A_{a\,3}$**	**$A_{b\,1}$**	**$A_{b\,2}$**	**$A_{b\,3}$**
I	0.008	0.003	0.003	0.003	0.002	0.003
II	0.003	0.004	0.002	0.003	0.003	0.004
III	0.004	0.006	0.006	0.004	0.004	0.003
VI	0.003	0.002	0.007	0.002	0.003	0.002
V	0.002	0.007	0.001	0.002	0.003	0.003
IV	0.003	0.002	0.002	0.003	0.002	0.002
Mean	**0.0037**	**0.0040**	**0.0035**	**0.0028**	**0.0028**	**0.0028**
Std. Deviation	**0.00214**	**0.00210**	**0.00243**	**0.00075**	**0.00075**	**0.00075**
±SEM	**0.00087**	**0.00089**	**0.00099**	**0.00031**	**0.00031**	**0.00031**

Company B:

Concentration of cadmium in white oil paint samples(%)						
	$B_{a\,1}$	**$B_{a\,2}$**	**$B_{a\,3}$**	**$B_{b\,1}$**	**$B_{b\,2}$**	**$B_{b\,3}$**
I	0.001	0.001	0.00	0.00	0.001	0.001
II	0.00	0.00	0.00	0.001	0.00	0.001
III	0.001	0.00	0.001	0.00	0.001	0.00
VI	0.00	0.00	0.001	0.001	0.00	0.00
V	0.00	0.001	0.00	0.00	0.001	0.001
IV	0.00	0.00	0.00	0.001	0.00	0.00
Mean	**0.0003**	**0.0003**	**0.0003**	**0.0005**	**0.0005**	**0.0005**
Std. Deviation	**0.00052**	**0.00052**	**0.00052**	**0.00055**	**0.00055**	**0.00055**
±SEM	**0.00021**	**0.00021**	**0.00021**	**0.00022**	**0.00022**	**0.00022**

Company C:

Concentration of cadmium in white oil paint samples(%)						
	$C_{a\,1}$	**$C_{a\,2}$**	**$C_{a\,3}$**	**$C_{b\,1}$**	**$C_{b\,2}$**	**$C_{b\,3}$**
I	0.001	0.002	0.002	0.001	0.002	0.000
II	0.002	0.001	0.001	0.003	0.001	0.001
III	0.002	0.001	0.000	0.002	0.001	0.002
VI	0.001	0.001	0.003	0.001	0.003	0.003
V	0.001	0.000	0.001	0.000	0.000	0.001
IV	0.001	0.001	0.000	0.003	0.001	0.002
Mean	**0.0013**	**0.0010**	**0.0012**	**0.0017**	**0.0013**	**0.0015**
Std. Deviation	**0.00052**	**0.00063**	**0.00117**	**0.00121**	**0.00103**	**0.00105**
±SEM	**0.00021**	**0.00026**	**0.00048**	**0.00049**	**0.00042**	**0.00043**

Company D:

Concentration of lead in white oil paint samples(%)						
	$D_{a\,1}$	**$D_{a\,2}$**	**$D_{a\,3}$**	**$D_{b\,1}$**	**$D_{b\,2}$**	**$D_{b\,3}$**
I	0.002	0.002	0.002	0.003	0.003	0.002
II	0.002	0.003	0.004	0.004	0.002	0.003
III	0.003	0.003	0.002	0.002	0.004	0.003
VI	0.004	0.004	0.003	0.003	0.003	0.003
V	0.003	0.003	0.004	0.003	0.003	0.002
IV	0.003	0.002	0.003	0.002	0.002	0.003
Mean	**0.0028**	**0.0028**	**0.0030**	**0.0028**	**0.0028**	**0.0027**
Std. Deviation	**0.00075**	**0.00075**	**0.00089**	**0.00075**	**0.00075**	**0.00052**
±SEM	**0.00031**	**0.00031**	**0.00037**	**0.00031**	**0.00031**	**0.00021**

Company E:

Concentration of lead in white oil paint samples(%)						
	$E_{a\,1}$	**$E_{a\,2}$**	**$E_{a\,3}$**	**$E_{b\,1}$**	**$E_{b\,2}$**	**$E_{b\,3}$**
I	0.002	0.002	0.001	0.002	0.004	0.002
II	0.001	0.003	0.003	0.003	0.002	0.003
III	0.002	0.001	0.002	0.004	0.003	0.003
VI	0.001	0.002	0.001	0.002	0.003	0.002
V	0.001	0.001	0.001	0.003	0.002	0.004
IV	0.003	0.001	0.002	0.003	0.004	0.003
Mean	**0.0017**	**0.0017**	**0.0017**	**0.0028**	**0.0030**	**0.0028**
Std. Deviation	**0.00082**	**0.00082**	**0.00082**	**0.00075**	**0.00089**	**0.00075**
±SEM	**0.00033**	**0.00033**	**0.00033**	**0.00031**	**0.00037**	**0.00037**

Appendix section 3: Chromium in white oil paint samples

Company A:

Concentration of chromium in white oil paint samples(%)						
	$A_{a\,1}$	**$A_{a\,2}$**	**$A_{a\,3}$**	**$A_{b\,1}$**	**$A_{b\,2}$**	**$A_{b\,3}$**
I	0.003	0.004	0.001	0.005	0.004	0.006
II	0.004	0.003	0.004	0.007	0.005	0.008
III	0.004	0.002	0.003	0.006	0.008	0.007
VI	0.004	0.003	0.004	0.008	0.007	0.005
V	0.002	0.002	0.002	0.004	0.006	0.007
IV	0.001	0.004	0.003	0.006	0.006	0.004
Mean	**0.0030**	**0.0030**	**0.0028**	**0.0060**	**0.0060**	**0.0062**
Std. Deviation	**0.00126**	**0.00089**	**0.00117**	**0.00141**	**0.00141**	**0.00147**
±SEM	**0.00052**	**0.00037**	**0.00048**	**0.00058**	**0.00058**	**0.00060**

Company B:

Concentration of chromium in white oil paint samples(%)						
	$B_{a\,1}$	**$B_{a\,2}$**	**$B_{a\,3}$**	**$B_{b\,1}$**	**$B_{b\,2}$**	**$B_{b\,3}$**
I	0.001	0.001	0.001	0.001	0.000	0.000
II	0.001	0.001	0.001	0.001	0.000	0.001
III	0.002	0.001	0.002	0.00	0.001	0.000
VI	0.001	0.001	0.001	0.001	0.000	0.001
V	0.001	0.002	0.001	0.00	0.001	0.000
IV	0.002	0.001	0.002	0.00	0.000	0.000
Mean	**0.0013**	**0.0012**	**0.0013**	**0.0005**	**0.0003**	**0.0003**
Std. Deviation	**0.00052**	**0.00041**	**0.00052**	**0.00055**	**0.00052**	**0.00052**
±SEM	**0.00021**	**0.00017**	**0.00021**	**0.00022**	**0.00021**	**0.00021**

Company C:

Concentration of Chromium in white oil paint samples(%)						
	$C_{a\,1}$	**$C_{a\,2}$**	**$C_{a\,3}$**	**$C_{b\,1}$**	**$C_{b\,2}$**	**$C_{b\,3}$**
I	0.001	0.001	0.001	0.001	0.001	0.002
II	0.000	0.001	0.001	0.001	0.001	0.001
III	0.001	0.000	0.000	0.001	0.001	0.001
VI	0.001	0.001	0.001	0.001	0.001	0.001
V	0.000	0.000	0.001	0.000	0.001	0.001
IV	0.000	0.010	0.000	0.000	0.001	0.000
Mean	**0.0007**	**0.0005**	**0.0005**	**0.0008**	**0.0010**	**0.0010**
Std. Deviation	**0.00082**	**0.00084**	**0.00084**	**0.00075**	**0.00063**	**0.00063**
±SEM	**0.00033**	**0.00034**	**0.00034**	**0.00031**	**0.00026**	**0.00026**

Company D:

Concentration of Chromium in white oil paint samples(%)						
	$D_{a\,1}$	**$D_{a\,2}$**	**$D_{a\,3}$**	**$D_{b\,1}$**	**$D_{b\,2}$**	**$D_{b\,3}$**
I	0.002	0.002	0.003	0. 002	0.004	0. 002
II	0.003	0.003	0.002	0. 002	0.001	0.001
III	0.002	0.002	0.001	0. 001	0.003	0.002
VI	0.003	0.002	0.001	0. 003	0.002	0.003
V	0.001	0.003	0.003	0. 002	0.003	0.003
IV	0.002	0.002	0.002	0. 003	0.002	0.001
Mean	**0.0022**	**0.0023**	**0.0017**	**0.0022**	**0.0025**	**0.0017**
Std. Deviation	**0.00075**	**0.00103**	**0.00049**	**0.00075**	**0.00055**	**0.00121**
±SEM	**0.00031**	**0.00042**	**0.00042**	**0.00031**	**0.00022**	**0.00049**

Appendix section4: Lead in pigment samples

	Concentration of lead in pigment samples µg/Kg			
	F	**G**	**H**	**I**
I	85.10	52.34	77.90	46.62
II	86.50	54.10	77.52	43.65
III	86.58	53.90	77.86	45.51
Mean	**86.0600**	**53.4467**	**77.7600**	**45.2600**
Std. Deviation	**0.83235**	**0.96360**	**0.20881**	**1.50070**
±SEM	**0.48056**	**0.55634**	**0.12055**	**0.86643**

Appendix section 5: Cadmium pigment samples

	Concentration of cadmium in pigment samples µg/Kg			
	F	**G**	**H**	**I**
I	13.82	11.57	29.73	1.83
II	13.95	11.83	29.65	1.84
III	13.86	11.74	29.43	1.86
Mean	**13.8767**	**11.7133**	**29.6033**	**1.8433**
Std. Deviation	**0.06658**	**0.13204**	**0.15535**	**0.01528**
±SEM	**0.03844**	**0.07623**	**0.08969**	**0.00882**

Appendix section 6: Chromium pigment samples

	Concentration of chromium in pigment samples µg/Kg			
	F	**G**	**H**	**I**
I	32.85	41.75	1.52	2.82
II	32.46	41.52	1.56	2.79
III	32.61	41.38	1.53	2.84
Mean	**32.6400**	**41.5500**	**1.5367**	**2.8167**
Std. Deviation	**0.19672**	**0.18682**	**0.02082**	**0.02517**
±SEM	**0.11358**	**0.10786**	**0.01202**	**0.01453**

Appendix section 7: Statistics

Formulas used to calculate Mean ($X_{avr.}$), Standard Deviation (SD) and Relative Standard Deviation% (RSD%) in this document are given below:

$X_{avr.}$ = $\Sigma x_i / n$

SD = $\surd$ [$\Sigma(x_i - x_{avr.})2 / (n-1)$]

RSD% = (SD / $X_{avr.}$)*100%

where:

x_i = Individual data

n = number of samples

Appendix section 8

The X-ray fluorescence S2 RANGER is energy-dispersive X-ray fluorescence (EDXRF) spectrometer.

Appendix section 9

A Shimadzu model AA-6800 Series atomic absorption spectrophotometer , graphite furnace atomic absorption spectrophotometer (GFAAS).

Arabic Abstract

النتائج المتحصل عليها من خلال هذه الدراسة من قياس بعض العناصر الضئيلة (الرصاص، الكادميوم و الكروم) في الطلاء الأبيض الزيتي الذي جمع من 5 شركات في مدينة بنغازي بأرقام تشغيله مختلفة نظرا لأهميتها في عملية التلوث البيئي. وكذلك قدرت هذه العناصر في عينات الصبغات ملونة متحصلة عليها من شركات اجنبية.

حللت عينات الطلاء الأبيض الزيتي في هذه الدراسة باستخدام تقنية طاقة تشتت الأشعة السينية المفلورة (EDXRF) وعينات صبغات ملونة (الأزرق – الأصفر- الأحمر –الأخضر) باستخدام تقنية مطياف الجرافيتي الامتصاص الذري (GFAAS).

وجد إن المنتجات الليبية (الشركات) الخاصة لإنتاج الطلاء الليبي وخاصة التي أقيمت عليها دراستنا في مدينة بنغازي تحمل نسب تراكيز مختلفة من شركة لأخرى؛ كما ان النسب تختلف باختلاف رقم التشغيلة (Serial number) حيث ان كل شركة تحتوي على عدة أرقام تشغيلة تختلف باختلاف تاريخ خلطها وتاريخ طرحها في الأسواق، وكان تركيز مدى هذه العناصر كالتالي: الرصاص (292ملجم/كجم-998 ملجم/كجم) والكادميوم (3 ملجم/كجم - 38 ملجم/كجم) والكروم (0 ملجم/كجم – 61 ملجم/كجم) معظم هذه التراكيز لم تتجاوز الحدود المسموح بها.

في هذه الدراسة وجد ان الشركات (A, B and D) لها التركيز في الطلاء الأبيض الزيتي نفسه في رقمي تشغيلة في كل العناصر الضئيلة (الرصاص والكادميوم والكروم) وهذا مايدل على إن هذه الشركات لها ليس مراقبه جودة في منتجاتها.

في قياسنا الشركة E, وجد اختلاف فى تركيز العناصر الضئيلة بين رقمي التشغيلة لهذه الشركة وهذا يدل على ان هذه الشركة ليس لها مراقبه جودة بين منتجاتها، بينما وجد ان الشركة C لا يوجد اختلاف بين تركيز العناصر الضئيلة اى إن هذه الشركة لها مراقبة جودة منتجاتها.

في هذه الدراسة وجد إن كل نتائج الرصاص المتحصلة عليها في الطلاء الزيتي الأبيض كانت أعلي من المواصفات القياسية الصينية التي تنص على إن الرصاص يجب أن لا تتجاوز الحد) ولكن معظمها لم تتجاوز الحد المسموح به في المواصفات (90 ppmالمسموح به 0.009% القياسية الليبية 0.06 %600 ppm)).

كل نتائج الكادميوم المتحصلة عليها في الطلاء الأبيض الزيتي في هذه الدراسة كانت أقل من 75) و الكروم كانت أقل من المواصفات القياسيه الصينيه ppmالمواصفات القياسيه الصينيه (60). ppm)

من خلال دراستنا اتضح إن تراكيز العناصر الضئيلة في الأصباغ (الرصاص، الكادميوم والكروم) أقل من الطلاء الأبيض الزيتي كما هو موضح فى مناقشة النتائج، وجد إن تركيز الرصاص فى الأصباغ يعتمد على لون الصبغة كالتالي:

الأصفر <الأخضر<الأحمر < الأزرق

(الصبغة الحمراء) لاحتوائها على أكسيد H تركيز الأعلى عنصر الكادميوم تبين فى العينة (الخضراء) تحتوى على أعلى تركيز الكروم من الصبغات Gالكادميوم فى منتجاتها، والعينة الأخرى .

ومن خلال النتائج المتحصلة عليها للعناصر الضئيلة من الأصباغ وكانت أقل من الحد المسموح به.

التوصيات

1- تطبيق مواصفات قياسية ليبية خاصة بالطلاء ومعتمدة من المواصفات القياسية العالمية لتراكيز العناصر الثقيلة لطلاء.

2- يجب على الشركات تصنيع الطلاء إجراء اختبارات التحليلية اللازمة للمواد الخام للتأكد من مطابقتها للمواصفات القياسية.

3- عند طلاء المنازل يجب التهوية الجيدة لمدة لا تقل عن 48 ساعة بعد عملية الطلاء.

4- الأخذ في الاعتبار عملية إعادة التصنيع والتخلص من المخلفات بطريقة أمنة و بذل أقصى الجهود لتقليل الانبعاث و النفايات خلال عملية التصنيع .

كلية العلوم **جامعة بنغازي**

قسم الكيمياء

تقدير بعض العناصر الضئيلة في الطلاء الزيتي الأبيض والأصباغ

لإكمال متطلبات الحصول على الإجازة العليا
(الماجستير)

مقدمة من الطالبة:

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بنغازي- ليبيا

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