UNIVERSITY OF NAIROBI

EVALUATION OF LEAD, CADMIUM, AND CHROMIUM LEVELS IN AUTOMOTIVE PAINTS IN KENYAN MARKET

BY

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DECLARATION

I declare that this thesis is my original work and has not been submitted elsewhere for research. Where other people's work or my own work has been used, this has properly been acknowledged and referenced in accordance with the University of Nairobi's requirements.

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DEDICATION

This thesis is dedicated to God Almighty, friends and my loving parents for their support throughout my study.

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ABSTRACT

Heavy metals such as chromium, lead and cadmium are added to paint because of their beneficial properties. Some of the compounds of chromium and cadmium are added to paints to provide protection against corrosion and for reflective properties while lead provides decorative colours, enhanced drying time and prevents corrosion of metallic surfaces. These heavy metals are however toxic even at low concentrations and are responsible for quite a number of health effects due their accumulation in the body more so to the automobile paint sprayers and are persistent in the environment.This study was conducted to assess the levels of lead, chromium and cadmium in automotive paints frequently used by automotive paint sprayers in Nairobi City. A total of thirty-two (n = 32) cans of automotive paints consisting of 4 sets of red, blue, green and white colours were obtained from each of the four formal and informal retail shops. The levels of lead, chromium and cadmium in the paint samples were analysed using Atomic Absorption Spectrophotometer after the digestion of the samples according to the standard procedures. The study revealed that all the automotive paint samples from informal retail shops had total lead levels above 90 ppm set limit according to the Kenya Bureau of Standards (KEBS). The mean levels of lead ranged from 221.0±1.4 ppm to 2688.4±19.5 ppm. Lead levels were comparatively lower in the formal than informal retail shops, although only one out of sixteen samples from formal retail had lead levels of 83.3±2.2 ppm that fell within the stipulated limit. The other samples from the formal retail shops had concentrations ranging from 115.6±16.1 to 555.2±36.1 ppm with white colour having the lowest concentrations and green colour having the highest. In the case of chromium, the levels ranged from 120.5±10.6 to 2771.9±35.6 ppm with only two paint samples out of sixteen from formal retail shops having chromium levels of 39.3±7.0 and 94.8±8.1 ppm that was within the recommended limit of 100 ppm according to European Union while the rest of the paint samples from the informal and formal retail shops exceeded this limit.. Cadmium levels in paint samples from informal retail shops ranged from 2.4±1.5 to 12.5±0.6 ppm while those from formal retail shops ranged from 7.5±0.3 to 24.8±0.1 ppm. In both formal and informal retail shops blue colour had the lowest cadmium concentrations while green colour had the highest concentrations. It was observed that some automotive paint samples from formal retail shops had higher concentrations of cadmium than those from informal retail shops. However, concentrations of cadmium in all the automotive paint samples were below the set limit of 100 ppm. The results showed that automotive paints sold on the Kenyan market from both the informal and formal retail shops contained lead and chromium levels that were of health and environmental concern however the levels of cadmium were within the set limit. Therefore, there is urgent need to enforce the set standards to ensure the lead and chromium paints sold on the Kenyan market are within the required standards and that automotive spray painters are made aware of the adverse health effects associated with these paints.

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LIST OF ABBREVIATIONS AND ACRONMYS

AAS	Atomic Absorption Spectrometry
ATSDR	Agency for Toxic Substances and Disease Registry
CDC	Centers for Disease Control
DHHS	Department of Health and Human Services
EDTA	Ethylenediaminetetraacetic acid
ED-XRF	Energy Dispersive X-ray Flouroscence
GAELP	Global Alliance to Eliminate Lead in Paints
KEBS	Kenya Bureau of Standards
ICCM	International Conference on Chemicals Management
ILSG	International Lead and Zinc Study Group
NIOSH	National Institute of Occupational Safety and Health
PPE	Personal Protective Equipment
PPM	Parts per million
RoHS	Restriction of Hazardous Subtances
SD	Standard Deviation
TLVs	Threshold Limit Values
UNEP	United Nations Environment Programme
US	United States
UV	Ultra Violet
WHO	World Health Organization
WHSC	Workers Health Service Centre
XRF	X-ray Fluorescence

CHAPTER ONE

INTRODUCTION

1.1 Background Information

The rapid development and urbanization in Kenya have contributed to the mushrooming of informal industries and settlements being witnessed in many parts of urban areas. Limited resources as well as lack of modern methods of technology are major contributors to the factors leading to high levels of pollution (Briggs, 2003). This is worse for informal sector workers particularly the automotive paint sprayers who rarely use suitable personal protective equipment (PPE). The spray painters working in open garages, also known as “Jua Kali’’ garages are exposed to various pollutants associated with spray painting (Appendix 1).

Lead, chromium and cadmium are some of the heavy metals that are of concern to the environment and human health. The World Health Organization (WHO) has reported related burdens of diseases resulting from exposure to heavy metals. For instance, WHO noted that 3% of cerebrovascular diseases in the world is as a result of lead poisoning (WHO, 2016). In the year 2016, lead poisoning caused about 540,000 deaths which largely occurred in the developing countries leading to 0.6% of the disease burden (WHO, 2016; Needleman, 2004). Workers can be exposed to heavy metals during automotive spray painting (Mwatu, 2011). The activities of spray painting can also result in serious environmental contamination thereby increasing the risk of heavy metal exposure to communities in the immediate environment.

Basically, automotive paints are used for important functions that include esthetic value by providing protection and decoration of the metallic surfaces. Paints can be applied on metallic surfaces of automobiles such as cars, airplanes, trucks, buses, and motorcycles to offer ultraviolet protection, enhancement of color, fade, mold, heat, and moisture resistance. The paints contain a mixture of solvents, additives, and pigments which are used to impart color and opacity. They are referred to as thinners either in organic or water form which enhance the drying and hardening performance of the paint. Pigments and additives form emulsions and other mixtures and remain suspended in the systems because they do not dissolve completely (Turner, 1980). However, automotive paints have the ability to cause both environmental and human health problems. Lead, chromium, and cadmium are the major toxic pigments which can be found in automotive paints (IARC, 2010). Toxic metals are mostly contained in the paint pigments in form of lead chromate, chromate orange, lead oxide, chromate yellow, and cadmium yellow due to useful properties such as bright colours, fast drying and evenly distribution.

The initial preparation of the metallic surface involves intense sanding to remove the previous paints, prior to spray painting. This is also a potential source of exposure to heavy metals. The sanded-paint particles usually become airborne and are inhaled by those in the vicinity and some are deposited in the environment. There are different methods that are used to carry out spray painting. For instance, spray guns that use either a turbine or a compressor to produce tiny particles of air. At low pressure, the volume of the air flowing through the nozzle reduces the coating to a fine spray. Spray painting has been categorized as one of the activities that use high intensity of solvents exposure. Workers are usually exposed to elevated levels of the volatile and toxic substances containing heavy metals that are produced by the mists during spraying which end up in the surrounding environment (Abdalla *et al.*, 2016). They are therefore held for a long time in the air and can be inhaled by spray painters as well as those in their vicinities. The exposure time and concentration of heavy metals present in the automotive paints influences the toxicity of levels.

According to Vitayavirasuk *et al.* (2005), lower levels of exposure to heavy metals can induce organ damage since the metals are considered systematic toxicants. Many of the substances used in the manufacture of automotive paints are toxic to humans. These toxicants can cause irritations or burns to the skin, nose, eyes and throat which can lead to other symptoms such as dizziness, nausea and, or headaches. The symptoms are most times mild and can subside, reduce or even disappear once the immediate exposure has been stopped. Nonetheless, heavy metals are highly toxic since they bio-accumulate in human biological systems are persistent in the environment.

Additives in paints consisting of isocyanates, lead, cadmium, and chromium are carcinogenic and require adequate ventilation in order to disperse or reduce the exposure levels (Bieleman, 2000). Even at low concentrations, different individuals have sensitivity, reactivity, and irritation levels which vary according to the different chemical contaminants. Heavy metals such as lead, chromium, and cadmium in paints have specific threshold limit values (TLVs) (NIOSH, 1978). This is because different exposure levels require diverse protection methods. It therefore, calls for the use of appropriate PPEs when handling paints during the processes of spraying.

Lead is a toxic metal and when exposed to children and unborn babies it causes devastating health effects. Neurological, cardiovascular, and renal systems are some of the body systems that are adversely affected by lead poisoning. Exposure to lead is also known to result in intellectual disabilities among children (WHO, 2010). The International Conference on Chemical

Management (ICCM) held in 2009, identified lead paint as an emerging human health and environmental policy issue. It was in this context that the UNEP and WHO were tasked to provide leadership and form cooperation with diverse stakeholders to get rid of lead paint and create a healthy and habitable environment (GAELP, 2011). It is out of this effort that the Kenya Bureau of Standard (KEBS) recently established 90 ppm as the allowable maximum total lead content in paint and allied products that are sold in the Kenyan market (KEBS, 2018).

Another metal in automotive paint that is of considerable environmental and occupational concern is cadmium. The main route by which human being is exposed to cadmium is through inhalation during spray painting operations. Once cadmium is inhaled, it gets into the circulatory system as the distribution route and the vessels of blood are known to be the mainstream organs of cadmium toxicity (Nduka *et al.*, 2019). A study that was carried out by Schutte *et al.* (2008) found that reduction in mineral density of the bones and osteoporosis was as a result of chronic exposure to cadmium levels.

Hexavalent chromium, a component in paint, has been classified as a human carcinogen (Costa and Klein, 2006). The annual workplace exposure to compounds containing chromium was estimated to involve more than 300,000 workers (Goyer, 2001). Guertin (2005) noted that occupational exposure puts a lot of people around the world at the risk of developing chromium induced diseases. Workers in spray painting are therefore at risk of exposure at a higher magnitude than the general population (ATDSR, 2008). Environmental and occupational exposure to compounds containing hexavalent chromium is responsible for renal damage and respiratory tract cancer in humans (Goyer, 2001).

During spraying, the paint may also get into contact with the skin of the workers if not properly handled and when using inappropriate PPEs. Although skin contact may not be the main route of exposure for lead and cadmium it may contribute and enhance the overall body exposure when handling food with contaminated hands. On the contrary, chromium exposure to the skin may cause dermatitis and allergies (Vitayavirasuk *et al.*, 2005). Asthma and skin dermatitis are the primary diseases associated with spray painting activities (Mwatu, 2011). It is important that during manufacturing and formulation of paints addition of heavy metals should be controlled by using the established standards.

This study is therefore aimed at assessing the levels of lead, chromium, and cadmium in automotive paints sold in the Kenyan market and comparing the concentrations with the set standards in order to establish the extent of compliance. The data obtained will be useful in assessing the extent to which the users of these paints are exposed to health hazards arising from lead, cadmium, and chromium during spray painting. Besides, the study will assist in the structuring of policies and providing suitable recommendations to reduce exposures among spray painters. It will also assist in the enforcement of the established standards.

1.2 Statement of the problem

Automotive paints are usually applied to the metallic surfaces of automobiles for the purpose of protection and decoration. However, the presence of heavy metals such as Pb, Cd and Cr in automotive paints is of health concern to humans and the environment because of their toxicity even at low levels (Tichounwou *et al.*, 2012). The spray painters in informal garages are the most vulnerable groups due to lack of resources and appropriate protective equipment subjecting them to high levels of toxic metals exposure. The existence of many informal garages in Kenya suggests that several automotive paint sprayers are exposed to heavy metals (Mwatu, 2011). Recently, the Kenya Bureau of Standards established 90 ppm as the maximum allowable limit of total lead content in paint to ensure that no manufacturers add leaded materials during the manufacturing processes (KEBS, 2018). On the other hand European Union established the threshold limit values (TLVs) for cadmium and chromium as 100ppm (EU, 2016). It is, therefore, necessary to assess the levels of chromium, lead, and cadmium in the automotive paints in the Kenyan market.

1.3 Objectives

1.3.1 General objective

The general objective of this study was to assess the levels of selected heavy metals in automotive paints sold in the Kenyan Market.

1.3.2 Specific objectives

The specific objectives of this study were:

i. To determine the levels of lead, chromium, cadmium and evaluate their safety in automotive paints obtained from the formal and informal retail shops in Nairobi County, Kenya.

ii. To evaluate compliance of automotive paints sold in Nairobi County with the regulatory standards.

1.4 Justification and significance of the study

The exposure of spray painters to lead, chromium, and cadmium mists in informal garages commonly known as "Jua Kali" in Kenya is of concern due to health hazards associated with these heavy metals. Many spray painters work in poor ventilated areas without proper PPEs and they could be inhaling substantial amount of these heavy metals as they carry out their daily work. Assessing the levels of these heavy metals in automotive paints is of utmost importance to the public health and environment due to possible exposure. It is expected that the study will generate useful information that could be used in creation of awareness among the spray painters on the dangers associated with spray painting. The study will also provide necessary information that will assist in compliance and enforcement of the standards to reduce exposure to heavy metals. The environmental regulations have prohibited/limited the use of heavy metals during the manufacturing process of automotive paints and therefore the study will be able to show the extent of compliance.

CHAPTER TWO

LITERATURE REVIEW

2.1 Composition of paints

Paints are colloids that consist of a mixture of dispersed particles of a certain phase (solid or liquid) in a continuous phase (liquid or a solid). The continuous phase does not always need to be different from the dispersed phase, for example, a liquid-liquid emulsion but the interfacial properties of the two phases will differ. The size of the dispersed colloidal matter may range from a few nanometers up to tens of micrometers (Bentley, 2001; Lambourne and Strivens, 1999).

Paint can be considered as any pigmented liquid that after being applied on to a substrate in a thin layer it converts to a solid film. The fundamental components of paints include base, pigment, filler, drier, binder, and thinner. The base that forms the body of paints is a fine solid substance and it is comprised of white lead, red lead, zinc oxide (zinc white), iron oxide, titanium white, aluminium powder, lithophone, and others. Its function is to make a film of the paint opaque, harder, elastic, and prevent the development of shrinkage cracks (Reisch, 2003).

Filler or extender is a pigment added in paint to make it more economical and to save the expense of the base. The filler changes the weight of paint and makes it more durable. Inert fillers are used to give different physical properties other than colour, i.e opacity or texture. The most used inert fillers or extenders are barites (barium sulphate), lithophone, silica, silicate of magnesia or alumina, whiting gypsum, charcoal, and so on, so essentially it forms part of the base (Fettis, 2008).

The binder is the oil that is blended with base. It holds the paint together and binds it onto the surface to which it is applied thus provides durability, toughness, and the waterproof characteristic of the paint. Moreover, it helps to homogenously spread the paint ingredients over the surface onto which it is painted. It is responsible for providing adhesiveness, binding pigment and gives the paint resistance properties which make the final coating intense and durable. The commonly available binder or a vehicle is linseed oil, tung oil, poppy oil, and nut oil. The thinner increases its spreading ability as it makes the paint applied thin. Solvent is usually a volatile substance, it evaporates thus provides and enhances properties such as smoothness, easy flow, and applicability (Freitag and Stoye, 2008).

The drier functions as an accelerator during the process of drying. It assimilates oxygen from the air and transfers it to the vehicle (linseed oil) in the paint film, which thus gets hardened. Colouring pigments are materials added to the paint to impart the desired shade of colour. Additionally, they are used to conceal the surface defects and protect the paint film by reflecting the ultraviolet light and improve the impermeability. It also plays an intergral role in determining colour and appearance (Bentley, 2001).

When the solvent evaporates from paint, a coating is formed on the surface of the metal and thus the paint exhibits a two-phase system of mainly solids dispersed in a liquid. Paint is either oil-based or water-based which means that the paint's main ingredient is either water or a type of oil which could be either alkyd or linseed oil (Freitag and Stoye, 2008). The formulation of the coating could reduce the amounts of solvents being used and potentially hazardous components of paint. The process of drying is usually slow and this can be accelerated by adding driers to the paint which is based on the oxidation curing resin; namely oils, varnishes, alkyds, and modified alkyds. The widely used driers are naphthenates of lead, cobalt, and manganese. The driers also contain toxic heavy metals and can be a health hazard to human beings. For instance, lead is an accumulative poison and is known to be carcinogenic and therefore lead driers when present in the paint can cause poisoning of the liver and other internal organs of the human body (Bentley, 2001). According to Ishola *et al*. (2017), the major toxicants found in automotive paints include lead, cadmium, and chromium.

2.2 Automotive paints

Automotive paint is applied on the automobiles surfaces in several layers after some preparations and primer steps must be carried out. In general the automotive paint has two major purposes: to make automobiles look attractive and to protect the underlying metal or synthetic body panels from the harsh conditions of the environment (Fettis, 2008). Often, they are grouped into two broad categories: lacquers and enamel based on the difference in their consistency and application. Enamel is thicker than lacquers when mixed for spraying and are applied with thicker but fewer coats. The most widely used paint currently is the water-based acrylic polyurethane enamel paint. The first coat to be applied is called the primer and it serves as a leveler making the surface smoother, protects the vehicle from corrosion, heat and improves ease of application by making it easier to hold onto the surface. The base coat is then applied and it contains the effects and visual properties of colour. It’s normally divided into three categories: solid, metallic, and pearlescent pigments. Lastly, a clear coat is usually sprayed last atop the pigmented base coat, and in the final interface, it creates a shiny transparent coating. The clear coat has to be sturdy enough to withstand abrasion and chemically stable enough to hold out against the ultraviolet light rays (Streitberger and Dossel, 2008).

2.3 Types of automotive paints

The lacquer based and enamel are common forms of automotive paints (Streitberger and Dossel, 2008).

2.3.1 Lacquer based automobile paints

Lacquer based paints flow smoothly and dry very quickly. However, these paints are thin and provide very little ultraviolet resistance and they are therefore coated on the top surface with acrylic urethane in order to have a prolonged layer of protection giving a glossy finish. It is the most sought after automobile paint and is mostly used on luxury vehicles as they leave a glossy finish once they dry. The painted surfaces gets less dust and dirt as it dries faster but should nevertheless be buffed in order to have a shiny finish for a very long time.

2.3.2 Enamel paints

Due to heavier body, these paints dry forming very hard surface making them more durable. They provide magnificent coverage and outstanding retention of colour. They accord surfaces moisture, chip, and corrosion resistance as well as rust protective properties.

2.4 Properties of automotive paints

Ansdell (1999) stated that any paint of good quality is expected to fulfill the following properties:

i. Lightfastness - which describes how well it withstands degradation from UV light.

ii. Heat stability - the durability of the paint in the outdoor application does not depend upon its fade resistance in the sunlight. The resilience of color is rather much affected depending on how it withstands high temperatures.

iii. Opacity– gives the ability to completely conceal the surface that is being painted. The pigment can be selected based on either its hiding ability or its translucency.

iv. Chemical resistance – refers to a situation whereby the color can not only change but the hue also changes. Some pigments darken when either exposed to acids, alkali, and heat or air pollutants, as a result of oxidation or reactions to other elements present in the environment.

2.5 Formation of colour in automotive paints

Lead, cadmium, and chromium appear in the paint pigments in the form of lead chromate-yellow. lead oxide-white, lead-white, red lead, cadmium-yellow, cadmium-green, cadmium-red chrome-yellow, chrome-green, and chrome-orange (Buxbaum, 2008). Interaction between light and colorants (pigments and dyes) leads to the formation of diverse colours. Pigments reflect selectively and absorb specific wavelengths of visible light thus giving out certain colours whereby the appearance of a colour is created by the reflected light spectrum (Brill and Falk, 1981). This gives the paints brilliant colors. Some inorganic pigments, such as cadmium-yellow (cadmium sulfide), assimilate light by moving an electron from the negative ion (S^{2-}) to the positive ion (Cd^{2+}). The other parts of the spectrum or wavelengths are reflected or dispersed. The new reflected light spectrum creates the appearance of a colour. The other properties of a colour, such as its brightness may be determined by the other substances that accompany pigments. Binders and fillers which are added to pure pigment chemicals do have their own reflection and absorption patterns which can affect the final spectrum (Brill and Falk, 1981).

2.6 Health effects of heavy metals' exposure

Lead, chromium, and cadmium are the major toxic heavy metals that are added to automobile paints as components of the pigments. Heavy metals are elements that are metallic and aresknown to be toxic even at low concentrations. Generally, heavy metals are considered to have a density exceeding 5g/cm^3 (Jaishankar *et al.*, 2014). They can therefore lead to serious and adverse health effects with different kinds of symptoms depending on the quantity and the nature of the metal (lead, chromium and cadmium) being ingested or inhaled by the spray painters.

2.6.1 Lead

Lead (Pb) is a transition element that is considered a heavy metal with a density of 11.3 g/cm^3 (ATSDR, 2010). It is used in the manufacture of paints to increase the rate of the drying process, increase durability, retain a good appearance, and resisting moisture that may lead to corrosion on the automotive body parts. ILSG (2004) explains that the yellow, orange, red, and green colour in paints arise from lead carbonate and lead chromate.

Lead is classified as a poisonous metal and a cumulative poison. Paints are some of the most outstanding sources of lead in the environment (Gaitens *et al.*, 2008) with the common use of lead-based additives during the process of paint manufacture as the major contributor to lead in paints (Brokbartold *et al.*, 2012). Lead exposures occur when lead dust or fumes are inhaled. Poisoning from lead can cause a myriad of symptoms and signs which may vary depending on the individual and the duration of exposure (Karri *et al.,* 2008).

The process such as sanding of vehicle before spray painting emits substantial amount of lead in the environment (Mielke *et al*., 2001). In this case its not only spray painters that will be affected but children as well. Children are at a higher risk of lead poisoning because their smaller bodies are in a constant state of growth and development . A study conducted in recent times has shown that when children ingest small amounts of lead-based paints they suffer neurological damage (Woolf *et al.,* 2007). The Centre for Diseases Control (US) has set a maximum limit for lead in blood for adults at 10 µg/dl and children as 5 µg/dl (Dapul and Laraque, 2014). Authorities such as the American Academy of Pediatrics define lead poisoning when lead levels in the blood is higher than 10 µg/dl (Ragan and Turner, 2009). In the United States the current upper reference level for blood lead is 5 µg/dl. This reference was set in 2012 using the 97.5th percentile of blood levels in children aged 1 to 5 years in the National Health Nutrition and Examination Survey (Raymond and Brown, 2016).

Recent studies have also shown that high levels of lead in blood are associated with an increase in blood pressure and mortality (Chowdhury *et al.,* 2014). Pregnant women with high lead levels in blood are at a significantly high risk of spontaneous abortion. (Gidlow, 2015), premature birth or with a low birth weight. However, lead in blood is associated with reduced intelligence, attention, deficit hyperactivity disorder, hearing impairment, and delayed puberty in girls (Selevan *et al.*, 2003). Lead affects every system of the body in humans of which the brain is the most sensitive organ. The symptoms may include abdominal pains, headaches, and constipation, irritability, and memory problems whereby some of these effects are permanent, and in serious cases, it may cause anemia or death (Pearce, 2007; CDC, 2001; CDC, 2013).

Countries and different organizations have come up with lead-based paint limits in automotive paints. Kenya Bureau of Standards specifies the maximum allowable total lead content as 90 ppm in paints (KEBS, 2018). Global Alliance to Eliminate Lead Paint (GAELP) under the partnership of UNEP and WHO has a broad objective which is to gradually but ultimately phase out the manufacture and sale of paints containing lead and to eventually eliminate the risks and dangers associated with such paint (GAELP, 2011). This is by urging the government to implement the 90 ppm legal limit of lead in order to phase out lead in paint.

2.6.2 Chromium

According to Jacobs and Testa (2005) chromium (Cr) is a heavy metal that forms compounds using its five valence states that start with chromium (II) up to chromium (VI) which occurs in the earth's crust. It has a density of 7.19 g/cm^3. There is still widespread use of primer paint containing hexavalent chromium, in aerospace and automobile refinishing applications (Baselt, 2008). Hexavalent chromium pigments such as lead chromate are used in paints. Chromium oxides are also used as a green pigment and they are extremely lightfast and thus used in cladding coatings. It also forms the main ingredient in infrared reflecting paints used mainly by the armed forces to paint vehicles (Marrion, 2004). Hexavalent chromium is highly toxic and mutagenic when inhaled (Wise and Wise, 2012). Several regulatory agencies have classified it as a human carcinogen as it is a pollutant to human health and the environment (Achmad and Auerkari, 2017).

Hexavalent chromium is associated with several health hazards for example lung cancer, eye, skin, nose, and lungs irritation. Increasing the exposure duration to chromium compounds increases the vulnerability to lung cancer (ATSDR, 2012).

2.6.3 Cadmium

Cadmium is a heavy metal that appears either as a greyish-white powder or blue-white metal found in lead, copper, and zinc sulphide ores. It has a density of 8.65 g/cm^3. Cadmium compounds can be used in the production of paint pigments, dyes (cadmium sulphide, cadmium selenide commonly called cadmium red) in paints (Buxbaum and Ptaff, 2005). The most common means by which spray painters can be exposed to cadmium is through the inhalation of dust and fumes from sanding of metal surfaces before spray painting (Morrow, 2010). Breathing air which is highly contaminated with cadmium can lead to severe damage of the lungs and can lead to death while breathing of lowly contaminated air with cadmium leads to chronic poisoning (Hayes, 2007). Several studies had shown cadmium can induce liver damage (Baba *et al.*, 2013). Cadmium was banned in the market by the European Union’s Restriction on Hazardous substances (RoHS) (Morrow, 2010). The European Union limited its cadmium levels in paints at 100 ppm (EU, 2006).

2.7 Health hazards and symptoms associated with spray painting

Most studies have shown that small-scale industrial workers are more prone to workplace hazards, risks, and ill health effects (Adei *et al.*, 2011). For instance, during sanding processes spray painters are at high health risk due to exposure to heavy metals in paints (Tse *et al.*, 2011; Keski-santti *et al.*, 2010). Health hazards could be attributed to lack of protective gear, lack of knowledge, and awareness concerning the existing occupational health safety guidelines (Ahmad *et al.*, 2016). A study carried out in Nairobi by Mwatu (2011) showed that asthmatic symptoms, dermatitis, and eye problems were associated with spray painting activities in the informal garages. There are several health hazards and symptoms that could be experienced by spray painters.

2.7.1 Neurological symptoms

A study was carried out in the industrial suburbs of Khartoum, Sudan to identify the most exhibited neurological symptoms by the paint sprayers and their apprentices. The study revealed that most of the paint sprayers did not wear masks, gloves and proper protective clothing hence their bodies were exposed during their spraying leading to peripheral neuropathy (Abdalla *et al.*, 2016). Cadmium is a non-essential heavy metal and known carcinogenic (Luevano and Damodaran, 2014). It can enter the peripheral and central nervous systems through the nasal mucosa (Bishak *et al.*, 2015).

2.7.2 Asthmatic symptoms

Activity such as spray painting contain wide range of toxic heavy metals that can be inhaled by those in close proximity. Asthma is a worldwide health problem that affects millions of these workers (Chan-Yeung and Malo, 2005). Numerous researches conducted in the USA and Japan showed that about 75 percent of adult with asthma cases resulted from occupational exposure. Workers experience occupational asthma when they are exposed to fumes, vapor, gases, dust containing heavy metals during their daily spray painting activities (Baur *et al.*, 2012).

Paints containing chromates when inhaled by spray painters in the workplace lead to occupational asthma (Tarlo and Lemiere, 2014). After sometime, the airways of the workers' lungs become aggravated because of inhalation of the pollutants making them over sensitive and inflamed. Spray painting is one of the ways in which workers are exposed to pollutants that result in asthmatic and respiratory impaiments (Vitayavirasuk *et al.*, 2005). Control of exposure to asthma-causing agents is essential as it is life-threatening and can lead to death (Adei *et al.* ,2011). A death rate of 5.2 per 100000 population (0.7%) in 2010 globally has been reported (Vos *et al.*, 2010).

2.7.3 Skin dermatitis

A common health hazard associated with spray painting is skin dermatitis which can be caused by contact with paints containing the heavy metals. This can lead to unfavorably contact dermatitis and aggravation dermatitis bringing about ulceration of the skin which is also referred to as chrome ulcers (Basketter *et al.*, 2000). This condition is also known as occupational or industrial dermatitis since it is caused by coming into contact with a substance at the workplace (Hansen *et al.*, 2003). Contact dermatitis is normally instigated by external exposure of the skin to an allergen such as chromium; however, sometimes a systemically administered allergen may reach the skin through the circulatory system and thereby produce a systematic contact dermatitis (Nijhawan *et al.*, 2009; Kaukiainen *et al.*, 2005).

2.7.4 Eye irritation

Eye protection is very important especially when one is working in an environment that is likely to be a source of injury or hazardous to the eyes. Such an environment may be in an auto paint containing chemical pollutants such as cadmium and chromium which when one is exposed to, causes eye irritations, temporary blurred vision, and even cornea damage (Awodele *et al*., 2014).

2.7.5 Bronchitis disease

This is a harmful effect due to the inhalation of the chemicals in the paint through the mists or vapor during the spray painting. The exposure can occur either during manufacturing or painting activties. Inhalation and ingestion are both means through which cadmium can enter the body systems. Cadmium can disrupt biological systems even at low concentrations (Bernard, 2004). It leads to ulcerations and perforations of the nasal septum, chronic bronchitis, decreased pulmonary function, and other respiratory effects according to Bradshaw *et al.*, 1998.

2.7.6 Cancer

Spray painters have elevated risks of developing various types of cancers (Brown *et al.*, 2002). Lung and bladder cancer have been reported from those workers who are exposed to cadmium present in the air (Guha *et al.*, 2010; Nawrot *et al.*, 2006) The U.S Department of Health and

Human Service (DHHS) and the International Agency for Research on Cancer (IARC, 2004) reported that cadmium and associated compounds are human carcinogens.

2.8 Methods of heavy metal analysis in paints

Some of the common methods used in the heavy metal analysis in paints include; atomic absorption spectrometry (AAS), inductively coupled plasma mass spectroscopy (ICP-MS), energy dispersive X-ray fluorescence (ED-XRF) and X-ray fluorescence (XRF) (ASTM, 2004). In this study, the AAS technique was used because it is cheaper and readily available. The following section provides the theory on the working principles of atomic absorption spectrometry.

2.8.1 Atomic absorption spectrophotometry

The atomic absorption spectrometry is a process that employs the principle that free atoms in gaseous form such as Pb, Cr and Cd generated in the atomizer can absorb radiation at a specific wavelength specific to that element. The technique quantifies the absorption of atoms in the gaseous state whereby atoms absorb enrgy and make transitions from ground state to higher electronic energy states. This amount of absorption helps in determining the concentration of the Pb, Cr and Cd. It requires standards with known concentration of Pb, Cr and Cd to establish the relation between the measured absorbance and the analyte concentration which depends on the Beer-Lambert Law in which absorbance is directly proportional to the path length and concentration of Pb, Cr and Cd. This can be expressed as:

$$\mathbf{A} = \boldsymbol{\varepsilon}\, \boldsymbol{l}\, \boldsymbol{c} \qquad (2.1)$$

Where:

A is absorbance

ε is the molar attenuation coefficient or absorptivity of the attenuating species

l is the optical path length

C is the concentration of the attenuating species

The main components of atomic absorption spectrometer include spectral source, atom cell, monochromator, detector, amplifier, and display system for recording of absorption values. Schematic diagram of AAS is presented in Figure 2.1.

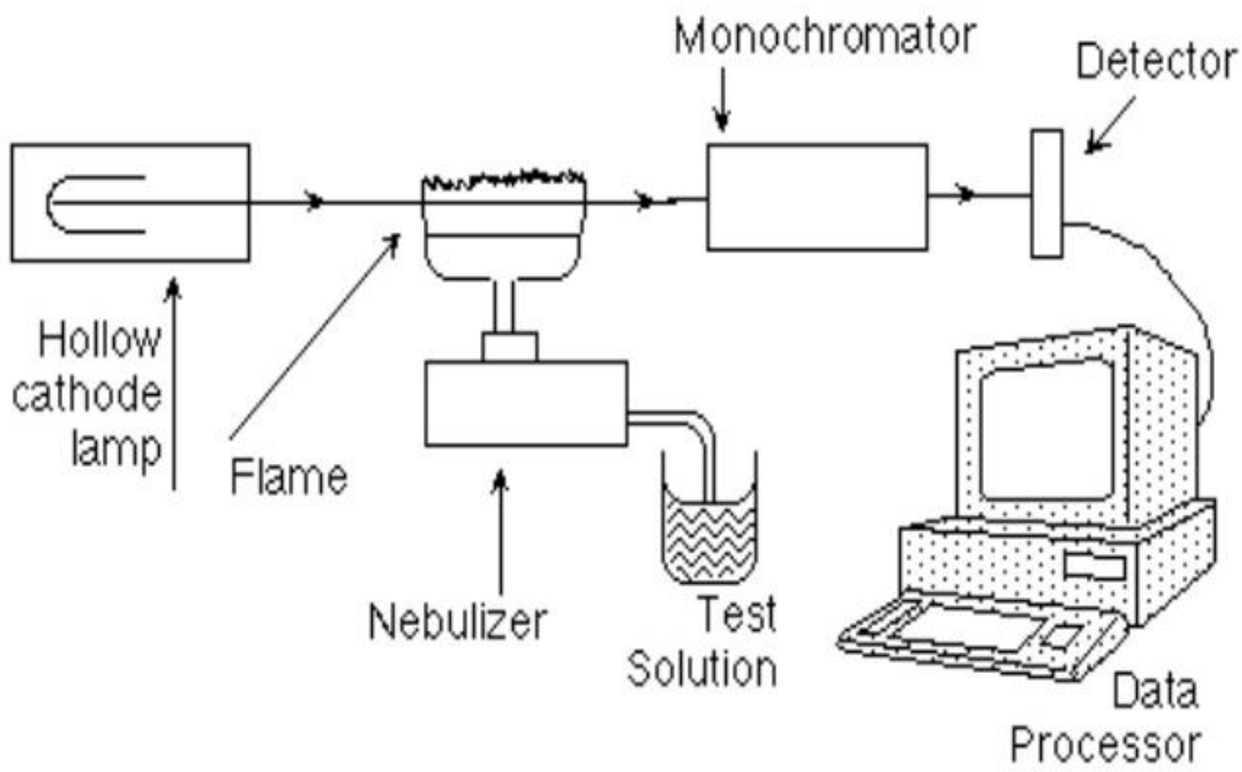


Figure 2. 1: A schematic diagram of an AAS
Source: Garcia and Baez (2012)

Hollow cathode lamp (HCL) – It consist of a glass tube with a cathode which is made with an element (metal) , an anode and a inert gas. Large voltage is applied such that when the metal is excited. Electrons from cathode travel at high speed towards the anode and in the process ionizes the inert gas (e.g $Ar \rightarrow Ar^+ + e^-$). The Ar^+ then travels at high speed towards the cathode and dislodges the metal of interest e.g Cd. It gains energy, gets excited and then retuns to the ground state with release of of energy. This is the energy used to excite Cd in the sample.

Nebulizer – It's a device that sucks up the liquid sample at a controlled rate. It creates a fine aerosol which mixes with fuel and oxidant. This gives negative pressure which creates suction for an uptake of liquid sample by a process of aspiration. The combustion gases flowing through the nebulizer draws the liquid sample into the flame as very fine droplets. Liquid sample that is not flowing in to the flame collects at the bottom of nebulizer chamber and flows by gravity and the waste is collected through a tube into a waste container.

Flame – The flame for AAS is produced when an oxidant and a fuel gas are mixed together. It is in the atomizer where the sample undergoes desolvation and vaporization at high temperatures. It breaks up complexes and creates the atoms of the element of interest. Combinations of the two gases that can be used includes air/acetylene where the air is the oxidant and acetylene is the fuel. In nitrous/acetylene it is the nitrous oxide which is oxidant and acetylene is the fuel.

Monochromator and detector – Monochromator isolates a single atomic wavelength from the lines emitted by the hollow cathode lamp excluding all the interfering lines and transmit it to the detector. Photomultiplier tube (PMT) is the most commonly used detector and it is used to determine the intensity of photons of the analytical line exiting the monochromator. The signal from the PMT is converted to the digital configuration by a transducer for read-out.The AAS has high sensitivity, selectivity, accuracy, precision, and speed, at which the analysis was done and thus used for the study.

2.9 Summary of gaps in knowledge

Studies performed on some decorative paints according to Kameti (2003) showed that almost all of the decorative paints used in Kenya contained high levels of lead that was above the recommended levels while cadmium levels were below the set limits. Assessment of levels of heavy metals in paints was carried out from interior walls and indoor dust from residential houses in Nairobi and it showed high levels of lead, chromium and cadmium (Ogilo *et al*., 2017). However, there was limited literature concerning lead, chromium and cadmium in automotive paints in the Kenyan market. This study thus fills the gap by assessing the levels of lead, chromium and cadmium in automotive paints. The use of proper protective gear during spraying has never been considered a priority in the informal garages, (Appendix 1).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Study area

The study area covered the formal and informal retail shops that sell automotive paints. The formal retail shops' location were mainly in the Industrial Area and Kariobangi North while the informal were located in Kamukunji and Kariobangi South in Nairobi County (Figure 3.1). Nairobi County lies between latitudes 1º15´S and longitudes 36º50´E with an area of 696 Km^2. The informal retail shops are the shops that sell small quantities of paints from 100 mL compared to formal shops that were selling from 250 mL. The informal retail shops that sold automotive paints were popular amongst paint sprayers since their paints were cheaper and commonly sold in small quantities to paint sprayers working in open garages. The open garages are mostly located within the residential areas and are usually adjacent to the retail shops that sold these paints.

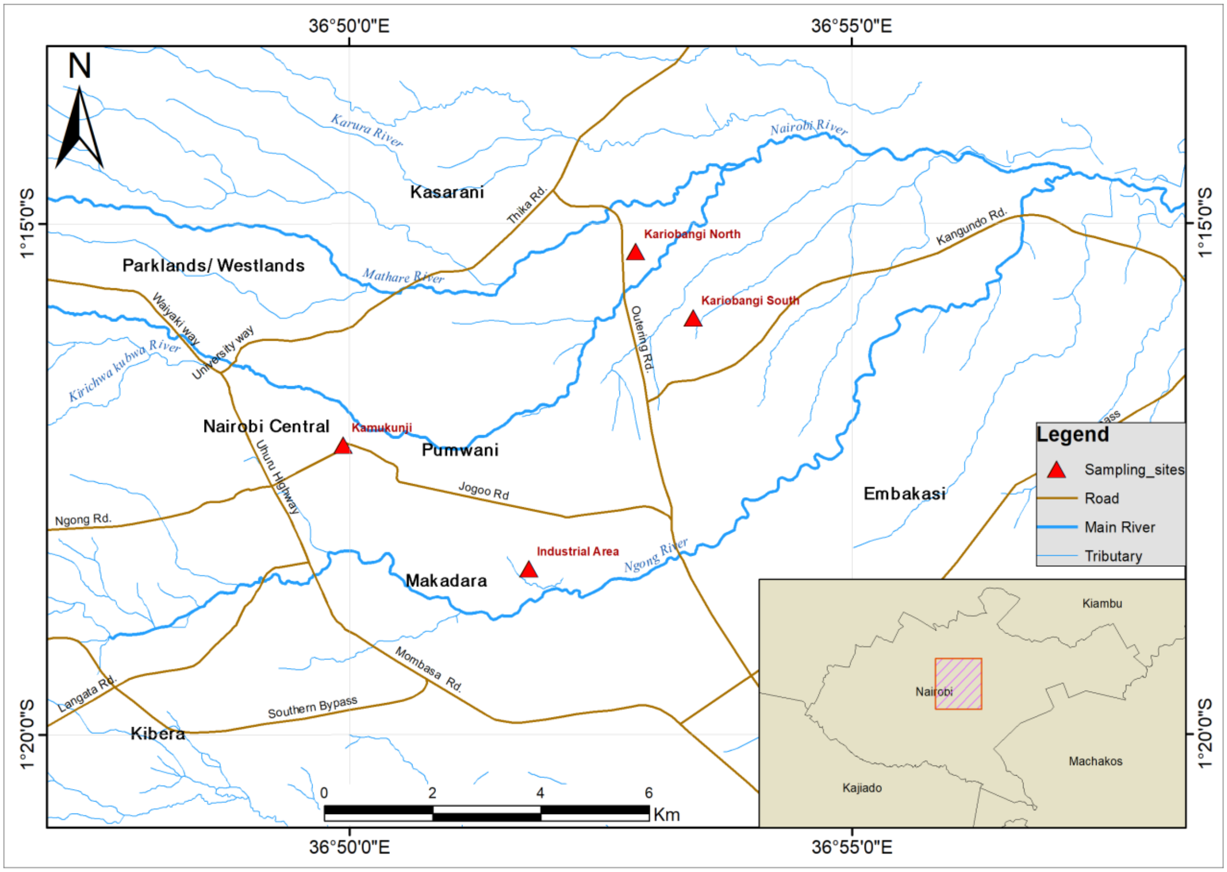


Figure 3. 1: Location of Informal and formal retail shops where paints are sold

3.2 Sampling and sample size

A total of 32 cans consisting of red, blue, green, and white colours of automotive paints were randomly purchased from four formal and four informal retail shops. The selection of the colours was based on the automotive paint colours that were frequently used by spray painters as they indicated in the questionnaire (Appendix 3) that was used to obtain the information from them. The colours that were listed by most of spray painters were red, blue, green and white. Four sets of cans of 250 mL of automotive paints that had red, blue, green, and white colours were obtained from each of the four formal retail shops in Industrial Area and Kariobangi North. Sets of 100 mL cans of automotive paints were purchased from four informal retail shops in

Kariobangi South and Kamukunji (Figure 3.1). The spray painters who were operating in the open garages usually buy the paints from those retail shops near their working places.

The paint samples were coded: FIA1, FIA2, FKN1, FKN2, IKS1, IKS2, IKA1, and IKA2 to represent the automotive paints that were purchased from the formal Industrial Area retail shop 1, formal Industrial Area retail shop 2, formal Kariobangi North retail shop 1, formal Kariobangi North retail shop 2, informal Kariobangi South retail shop 1, informal Kariobangi South retail shop 2, informal Kamukunji retail shop 1 and informal Kamukunji retail shop 2, respectively. The overall representative sample size of thirty-two (n=32) cans of automotive paint was therefore purchased. The code, colour, and year of manufacture of the paints were recorded as appropriate. All the 32 cans of paints were then transferred to the Mines and Geology Analytical Laboratory in the ministry of Mining for analysis of lead (Pb), chromium (Cr), and cadmium (Cd) concentrations.

3.3 Analysis of heavy metals in paints

Analysis of Pb, Cr, and Cd was carried out in accordance with ISO 6503 (1984) as described in the following procedure.

3.3.1 Sample preparation and digestion

Each of the thirty-two cans containing automotive paint samples was first homogenized by stirring the paints thoroughly then 0.5 g of the wet paint samples were placed into 500 mL conical flaks using plastic dropers and weighed in triplicates. The conical flasks containing the paint samples were thereafter placed on a hotplate in a fume chamber and heated gently to remove all volatile solvents for 5 minutes at a temperature of 200 ℃. The dried paint samples in the flasks were digested with 5ml sulphuric acid 96% v/v and boiled for 15 minutes to decompose and carbonize the organic substances until white fumes evolved. It was then allowed to cool for 10 minutes. This was followed by further additions of four 5 mL hydrogen peroxide 30% v/v allowing the reaction to subside after each addition.It was heated again for about 10 minutes and allowed to cool for 5 minutes. Two 5 mL portions of the hydrogen peroxide solution was added, heated for 5 minutes and allowed to cool for 5 minutes. Finally, one 5 mL portion of hydrogen peroxide solution was added and heated to decompose the remaining hydrogen peroxide. The conical flasks with the content were then heated until copious white fumes evolved and the solution evaporated to dryness. They were then removed from the hotplate and allowed to cool. The samples were then extracted by addition of 50 Ml EDTA (Ethylenediaminetetraacetic acid, disodium salt) of 37 g/L solution; 10ml of the ammonia solution 25% v/v, 50ml distilled water, and then boiled gently for 15 minutes (Appendix 2). The sample extracts were left to cool at room temperature and filtered using Whatman No. 42 filter paper into a 100 mL volumetric flask and topped up to the mark using distilled water for subsequent analysis. The blanks were prepared using the same procedure but with no sample added as appropriate for AAS analysis.

3.3.2 Preparation of standards and calibration curves

A series of working standards for lead (2 ppm, 4 ppm, 8 ppm, 10 ppm), chromium (1 ppm, 2 ppm, 4 ppm, 6 ppm, 8 ppm, 20 ppm), and cadmium (0.2 ppm, 0.5 ppm, 1 ppm, 1.5 ppm) were prepared from the standard stock solution of 1000 ppm in to a 50 mL volumetric flask using the procedure as shown in Appendix 4. They were used to generate the calibration curves for each metal analysed as presented in Appendices 5, 6, and 7.

3.3.3 Heavy metal analysis by Atomic Absorption Spectrophotometer

The standard, blank, and sample solutions were analyzed using AAS (Model: Shimadzu ASC-7000), (Appendix 8). The major instrumental parameters such as bandwidth, lamp current, flame temperature, and wavelength for AAS for each metal was optimized as given in Table 3.1

Table 3. 1: AAS optimum analytical conditions for the analysis of heavy metals

AAS Optimal Parameters			
Heavy metals	Pb	Cd	Cr
Lamp current (A)	10	8	10
Measurement time (sec)	1.0	1.0	1.0
Wavelength (nm)	283.3	228.8	357.9
Slit width (nm)	0.7	0.7	0.7
Flame type	Air-acetylene	Air-acetylene	Air-acetylene
Flow rate (Litres/minute)	2.0	1.8	2.8
Sensitivity limit (μg/g)	0.1100	0.0110	0.0550
Detection limit (μg/g)	0.0200	0.0006	0.0050

The concentrations of each of the metals (lead, cadmium, and chromium) in the test and blank samples were determined in parts per million (ppm) from AAS.

3.3.4 Quality Control and Assurance

Quality control and assurance were undertaken to ensure the reliability and accuracy of the results. This was carried out by thoroughly cleaning the glassware used in the analysis of samples. The glassware were thoroughly cleaned using 50% (v/v) nitric acid and rinsed with deionized and distilled water. Reagents used in this study were all of the analytical grades and distilled water was used in the preparation of all the solutions. The main instrumental parameters were set and optimized for each element analyzed. Calibration graphs of absorbance versus concentration were made together with blanks for each of the heavy metals samples analyzed at a linear regression of greater than 0.9892. The scooping of each coded paint sample was carried out using a plastic dropper as a single-use for each paint colour to avoid cross-contamination of the samples. After every ten samples that were analyzed a standard solution was aspirated to check the instrument drift. Inter-laboratory comparisons were also carried out for two samples from each retail shop using similar analytical procedures at the Mines and Geology and Analytical Laboratory in the Department of Chemistry of the University of Nairobi to determine the reliability and accuracy of the results. The levels of Pb, Cd, and Cr for samples selected for inter-laboratory comparisons showed a positive correlation of $r = 0.994$, $r = 0.999$, and $r = 0.999$ respectively.

3.4 Data analysis

Statistical data were analyzed using Microsoft Excel. The mean levels in parts per million (ppm) and standard deviation (sd) of lead, chromium, and cadmium were determined. The statistical significance of lead, cadmium, and chromium for automotive paints procured from formal and informal retail shops were determined by the student’s t-test. One-way variance of analysis

(ANOVA) was also carried out for the different colours in automotive paint samples procured from formal and informal retail shops.. The significance level was set at $p=0.05$ ($\alpha=0.05$).

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Lead levels in the automotive paints

The levels of lead in various colours of automotive paints that were purchased from the informal and formal retail shops are presented in Table 4.1. The informal retail shops were Kariobangi South Shop 1,Kariobangi South Shop 2, Kamukunji Shop 1 and Kamukunji Shop 2 (IKS1, IKS2, IKA1 and IKA2) respectively. The formal retail shops were Industrial Area Shop 1, Industrial Area Shop 2, Kariobangi North Shop 1 and Kariobangi North Shop 2 (FIA1, FIA2, FKN1 and FKN2) respectively.The lead levels for paint samples from each retail shop were calculated from the everage lead levels of the duplicate samples (Appendix:9) for different colours.

Table 4. 1: Levels of lead (ppm) in paint samples of different colours from informal and formal retail shops.

Sampled sites			Mean levels of lead (ppm) in various colours of automotive paints				Mean	Maximum Allowed Limit of Pb in paint (ppm) (KEBS, 2018)
			White	Blue	Red	Green		
Informal Retail Shop	Kariobangi South	IKS1	351.4±16.1	221.0±1.4	400.5±36.7	276.8±18.5	312.4±79.4	90
		IKS2	2386.1±68.1	399.6 ±8.9	2098.0±45.2	538.4±3.2	1355.5±1032.0	
	Kamukunji	IKA1	737.9 ±24.2	2688.4±19.5	712.9 ±20.3	800.1±8.6	1234.8±969.8	
		IKA2	1593.5±80.1	2651.2±77.3	857.6±5.1	2490.1±57.5	1898.1±835.3	
Mean			1267.2±908.7	1490.1±1364.3	1017.3±745.3	1026.4±998.9		
Formal Retail Shop	Industrial Area	FIA1	115.6±16.1	83.3±2.2	153.9±15.3	335.8±2.5	172.1±112.9	
		FIA2	196.7±6.6	150.7 ±5.2	233.2±28.4	327.7±6.6	227.0±75.1	
	Kariobangi North	FKN1	238.9±26.8	168.7±13.9	320.7±48.5	415.6±4.3	286.0±106.4	
		FKN2	327.8±9.6	277.2±4.3	344.7±18.3	555.2±36.1	376.2±122.7	
Mean			219.8±88.4	170.0±80.4	263.1±87.2	408.6±105.5		

The study showed that the levels of Pb in the paints from the informal retail shops ranged from 221.0±1.4 - 2688.4±19.5 parts per million (ppm) compared to those from the formal retail shops that ranged from 83.3±2.2 - 555.2±36.1 ppm. The high levels of lead could be contributed to the use of large amount of lead pigments and driers during paints formulation. In all cases, these levels exceeded the maximum limit of 90 ppm set by KEBS (2018) with exception of one paint sample that had a mean level of 83.3±2.2 ppm from the Formal Industrial Area retail shop 1

(FIA1). According to KEBS, (2018) technical report, paint manufacturers are capable of producing lead-free paint, with a total lead content of lower than 90 ppm by avoiding the use of leaded materials/pigments. From the results, levels of Pb in nearly all automotive paints from informal and formal retail shops exceeded the 90 ppm irrespective of the colour. This therefore suggested that paint manufacturers added leaded materials during the manufacture of paints.

The blue paint that was purchased from informal retail shop 1 in Kamukunji (IKA1) had the highest lead concentration of 2688.4±19.5 ppm, which was about 30 fold higher than the maximum allowable limit of 90 ppm total lead in paints. In contrast, the same quality of paint of blue colour from the formal retail shop 1 in the Industrial Area (FIA1) had the lowest Pb level of 83.3±2.2 ppm that was within the limit set by KEBS (2018). The second shop in the Industrial Area (FIA2) had similar quality of blue paint costing the same price (Appendix 10) but the level of lead (150.7±5.2 ppm) was higher than those of the first shop and exceeded the allowable limit by KEBS (2018). This, therefore, implied that the lead pigments and driers added differed in amount for each retail shops hence the difference in lead levels in the paints. This may not necessarily affect the cost of paints. The consequence of high lead concentrations in the paint is that spray painters have a high chance of inhaling high levels of lead which would expose them to health hazards during their daily operations. It should be noted that not only the spray painters that are affected by those motor vehicles' paintwork activities. The sanding activities of previously painted surfaces shown in Figure 4.1 contribute to extensive exposures and emissions of lead-containing particles to the environment and nearby communities (Mielke *et al.*, 2001). The work environment that is usually within the residential areas is highly contaminated. Lead is also one of the elements that is cumulative and persistent toxicant with no known biological function. It influences essentially every biological system within human body and has far-reaching consequences on health (Flora *et al*., 2006). Furthermore, the residue produced from sanding and spray painting activities can effectively stick to a paint sprayers garments and skin, and if not appropriately handled, it can spread around the working environment, and home exposing more people to adverse health impacts (Enander *et al*., 2002).

Figure 4. 1: Spray painting in an open garage adjacent to the Informal Retail Shop 1 in Kamukunji

Source: A photo taken during procurement of paint in April 2019

4.1.1 Lead levels in automotive paints sold in informal and formal retail shops

The lead levels in paints purchased from informal and formal retail shops were compared as shown in Figure 4.2. The lead levels were calculated from the everage of all the colours in each informal and formal retail shop. The first four bars (IKS1, IKS2, IKA1 and IKA2) represented paint samples from informal retail shops while the rest four represent paint samples from formal retail shops (FIA1, FIA2, FKN1 and FKN2).

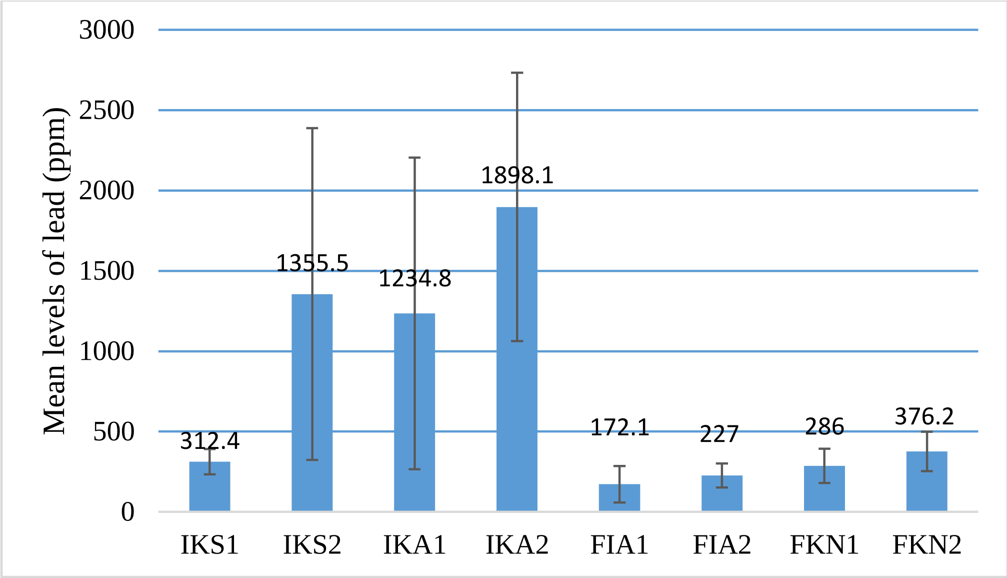


Figure 4. 2: Comparison of lead levels (ppm) in paint procured from different informal and formal retail shops

From the results presented in Figure 4.2, it is observed that paint samples procured from the informal retail shops (IKS1, IKS2, IKA1, IKA2) had the higher levels of Pb that ranged from 312.4±79.4 to 1898.1±835.3 ppm compared to those of the formal retail shops (FIA1, FIA2, FKN1, FKN2) that ranged from 172.1±112.9 to 376.2±122.7 ppm howevr paint from Informal Kariobangi shop 1(IKS1) had comparable lead levels with those of Formal Kariobangi shop 2 (FKN2). Among the informal retail shops, the paint samples from shop 2 in Kamukunji (IKA2) had the highest concentration followed by Informal Kariobangi South shop 2 (IKS2) samples, followed by Informal Kamukunji area shop 1 (IKA1) samples, while the lowest Informal Kariobangi South shop 1 (IKS1) samples. From the t-test carried out, lead levels for the samples from informal retail shops were not statistically different at $p > 0.05$, 95% confidence level. In almost all cases, the formal retail shops in the Industrial Area had the lowest mean levels of lead in paints compared to the retail shops in the Kariobangi North but there was no significant difference ($p > 0.05$) in the levels. The higher lead levels in paint samples from Kariobangi North could be attributed to the large amount of leaded materials that were used as a pigment and drying agent during paint preparation.

The P-value ($p < 0.05$) obtained from anova indicated that the difference in the lead levels from all the retail shops (formal and informal) was significant at 95% confidence level. These differences could be attributed to the addition of leaded materials during the manufacturing of the paints. High levels of lead in automotive paints observed in this study implied that users of paint will be exposed to high levels especially informal sector workers.

4.1.2 Lead levels in different colours of automotive paints

Lead levels in various colours are presented in Figure 4.3. The lead levels for white colour in informal and formal retail shops were calculated from the everage of all the white paint samples from informal and formal retail shops respectively. The same was done for the other colours (red, blue and green) and then they were compared as discussed below.

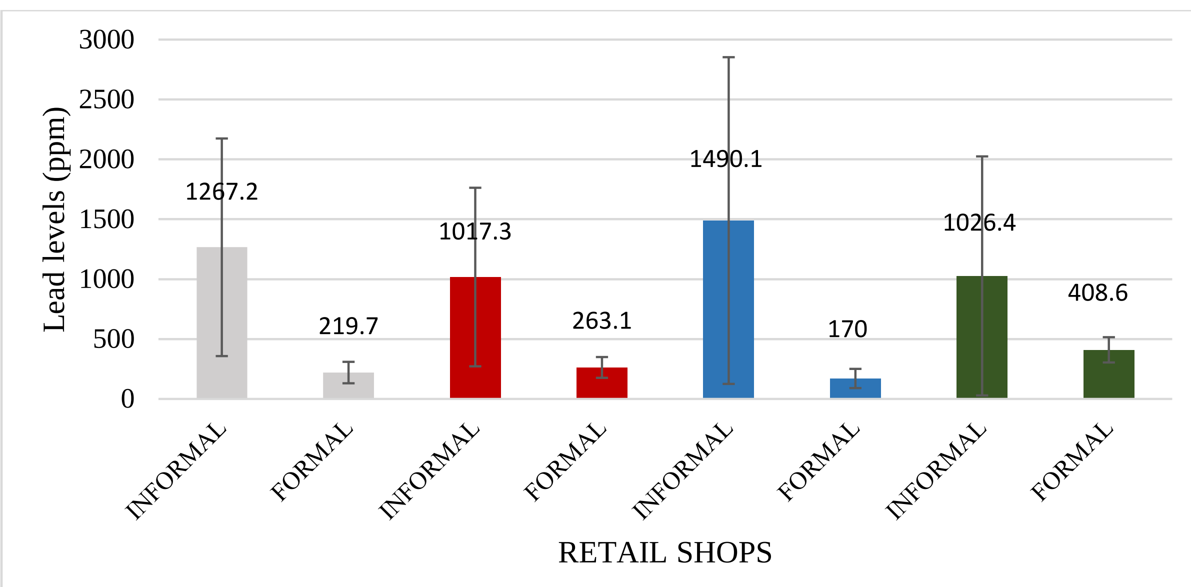


Figure 4. 3: Comparison of lead levels(ppm) in different colours of paint samples from formal and informal retail shops

From Figure 4.3, all the colours for automotive paints purchased from the informal retail shops had higher levels of lead compared to those from formal retail shops. This means that paints from informal retail shops could have been prepared with pigments and driers which contained high levels of lead. Irrespective of the location of procurement of the paint samples, the lead levels in the four colours (white, red, blue, green) from the formal and informal retail shops were not statistically different ($P > 0.05$) at 95% confidence level. It is observed that the levels of lead in informal retail shops was highest in blue colour (1490.1±1364.3 ppm), followed by white colour (1267.2±908.7 ppm), green colour (1026.4±998.9 ppm), and lastly red colour (1017.3±745.3 ppm) (Figure 4.3). Lead (II, IV) oxide also known as red lead or minium is the inorganic compound commonly used as a pigment in the manufacture of paint and can result in high concentration of lead in red paints (Higgit *et al*., 2003). This may explain the high levels of Pb that was observed in the red paint. The study indicated that spray painters that uses the red paint could be exposed to significantly high levels of Pb and if the standard is not being enforced.

In all the paint samples from formal retail shops, (Kariobangi South and Industrial area) the levels of lead were highest in green colour while blue colour had the lowest Pb levels (408.6±105.5 and 170.0±80.4 ppm), respectively (Figure 4.3). The P-value obtained from anova indicated that the levels were significantly different ($p< 0.05$). This is due to the fact that pigments used in paints are based on lead sulphochromate and molybdate lead chromate. The pigment lead chromate molybdate sulfate ($Pb (Cr, S, Mo)O_4$) is a variable blended phase crystal that contains lead chromate, lead sulfate, and lead molybdate in differing proportions (Buxbaum, 2008).

4.1.3 Lead level in paints from formal and informal retail shops

The lead levels in paints from formal and informal retail shops varied with the location of sampling and the colour of the paints. The lead levels for formal retail shops was calculated from the everage of all the paint samples purchased from formal retail shops (FIA1, FIA2, FKN1 and FKN2). This was also done for lead levels in informal retail shop paint samples (IKS1, IKS2, IKA1 and IKA2. Comparison of lead levels between formal and informal retail shops was done as discussed below.

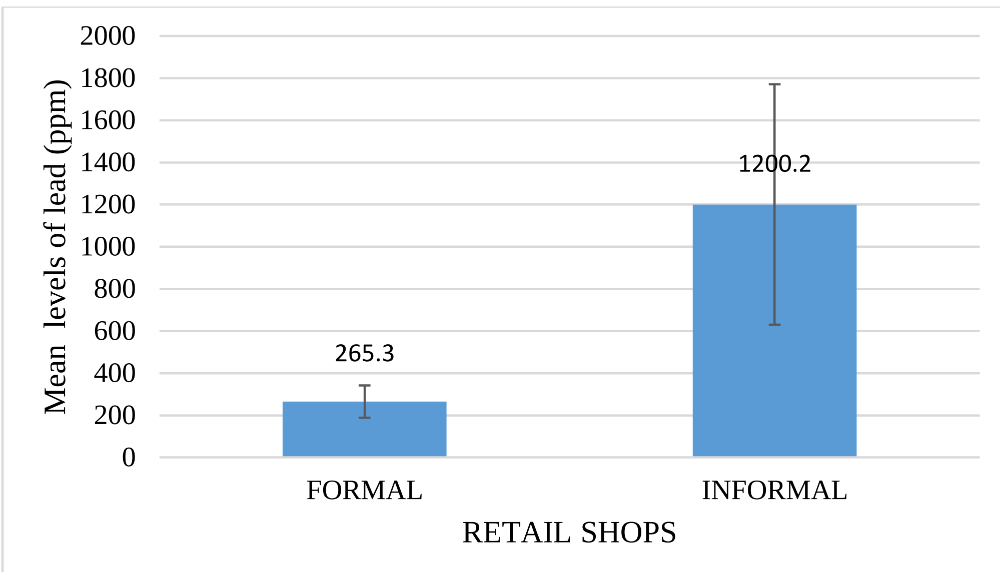


Figure 4. 4: Comparison of lead levels (ppm) in automotive paints from formal and informal retail shops

The formal retail shops had everage lead level 265.3±75.6 ppm while informal retail shops had everage lead level of 1200.2±570.2 ppm which was relatively high (Figure 4.4). A significant difference in lead levels was obtained from t-test analysis at 95% confidence level ($p < 0.05$). Lead compounds are added to paint as pigments to provide different colours and they include:

lead chromates (yellow), lead oxides (red), lead molybdates (orange), lead sulphates(white) among others (Volz *et al*., 2000). They can also be added for use as driers which act as catalysts that accelerate the polymerization making the paint dry faster and more evenly. Compounds that are used as driers include lead octoate and lead nephthenate. Compounds of lead for example, lead tetroxide are also added to paint so as to inhibit rust or corrosion (Bieleman, 2000). The lead compounds added by the paint manufacturers contribute to high concentrations of more than 90 ppm of lead in paints.

The implementation and enforcement of the established standards of phasing out lead in paint are most likely to be adopted by formal paint manufacturers since they have resources in research and development. The informal paint manufacturers who also run retail shops in the informal set up lacks resources and knowledge to make a shift to unleaded materials. The government should therefore support the informal sectors to shift to unleaded materials.

4.2 Chromium levels in automotive paints

Chromium levels for each informal retail shop (IKS1, IKS2, IKA1 and IKA2) and formal retail shop (FIA1, FIA2, FKN1 and FKN2) paint samples were calculated and are presented in Table 4.2. The maximum allowed limit of chromium in paint according to European Union is 100 ppm (Table 4.2).

Table 4. 2: Levels of chromium (ppm) in paint samples in different colours from formal and informal retail shops.

Sampled sites			Mean levels of chromium (ppm) in various colours of automotive paints				Mean	Maximum Allowed Limit of Cr in paint (ppm) (EU, 2016)
			White	Blue	Red	Green		
Informal Retail Shops	Kariobangi South	IKS 1	203.6±7.3	120.5±10.6	235.9 ±2.8	146.6±3.4	176.6 ±52.6	100
		IKS 2	2021.2±64.3	319.0±9.9	2380.5±6.2	406.9±1.8	1281.9±171.8	
	Kamukunji	IKA 1	512.6±14.4	2771.9±35.6	489.4±14.0	543.6±4.5	1079.4±128.6	
		IKA 2	657.8±5.6	1793.2±21.7	575.1 ±1.1	1350.6±38.0	1094.2±581.4	
Mean			848.8±804.2	1251.2±158.8	920.2±94.1	611.9±519.3		
Formal Retail Shop	Industrial Area	FIA 1	123.9±0.8	39.3±7.0	94.8±8.1	187.8±2.1	111.2±61.9	
		FIA 2	272.5±29.4	225.3±0.5	280.3 ±3.0	258.5±13.1	259.1±24.3	
	Kariobangi North	FKN 1	341.5±8.3	338.4±1.3	373.4±7.3	404.2±6.6	364.4±30.9	
		FKN 2	414.1±33.1	406.4 ±3.1	430.9±1.1	461.9±11.1	428.3±24.6	
Mean			288.0±123.7	252.4±160.5	294.9±147.1	328.1±126.8		

Out of sixteen samples from formal retail shops only two paint samples had chromium levels below the set limit of 100 ppm (EU, 2016). These are the samples that were obtained from Formal Industrial Area shop 1 (FIA1) in blue and red colour with concentration of 39.3±7.0 ppm and 94.8±8.1 ppm respectively (Table 4.2). Green and white colours had their levels above the set limit with concentrations of 187.8±2.1 and 123.9±0.8 ppm respectively. The samples from Formal Industrial Area Shop 2 (FIA2) had the highest levels in red colour (280.3±3.0 ppm) and lowest in blue colour (225.3±0.5 ppm) while the rest of the samples from Formal Shops (FIA1, FKN1, FKN2) had the highest and lowest concentration in green and blue colour samples respectively. Chromium (III) Oxide (green) is mostly used as a pigment in paint and therefore if added in large amount during paint formulation it could contribute to high levels of chromium in paint. The chromium levels were all above the set limit. T-test analysis showed that there was a significant difference in chromium levels in paints from formal compared to informal retail shops at $p<0.05$ and confidence level of 95%.

Samples from Informal Kariobangi South Shop 1 (IKS1) had the highest chromium levels of 235.9±2.8 ppm in red colour while the blue had the lowest concentration of 120.5±10.6 ppm. The same case with samples obtained from Informal Kariobangi South shop 2 (IKS2) which had concetration of 2380.5±6.2 ppm in red and 319.0±9.9 ppm in blue colour with no significance difference at $p>0.05$. The high chromium levels in red paints from Kariobangi South could be contributed by use of raw materials which contained Chromium (VI) Oxide which is mostly used during paint formulation to give the red colour. In Informal Kamukunji Area Shop 1 (IKA1) sample, the blue colour had highest chromium levels (2771.9±35.6 ppm) and lowest in red colour (489.4±14.0 ppm). Informal Kamukunji Area Shop 2 (IKA2) samples too had highest levels of chromium in blue colour 1793.2±21.7 ppm while red colour had the lowest with 575.1±1.1 ppm. Lead chromates are used as pigments to give a red colour and when used in higher percentage it could lead to high chromium levels in paints. Anova analysis showed that the levels of chromium in all samples procured from informal retail shops were significantly different at ninety five confidence level at $p<0.05$.

In the manufacture of anti-corrosive primer paints, various chromate pigments are often used. They include basic zinc chromate/alkali chromate, basic potassium zinc chromate, basic zinc chromate, strontium chromate, calcium chromate, and lead chromate (Otero *et al*., 2017). If the materials used in paint formulation contained this compounds this could lead to high levels of chromium in the automotive paints.

4.2.1 Chromium levels in automotive paints sold in formal and informal retail shops

The levels of chromium were calculated for the different informal and formal retail shop paint samples. The first four bars represent paint samples purchased from informal retail shops (IKS1, IKS2, IKA1 and IKA2) while the rest represent paint samples from formal retail shops (FIA1, FIA2, FKN1 and FKN2) which were then compared.

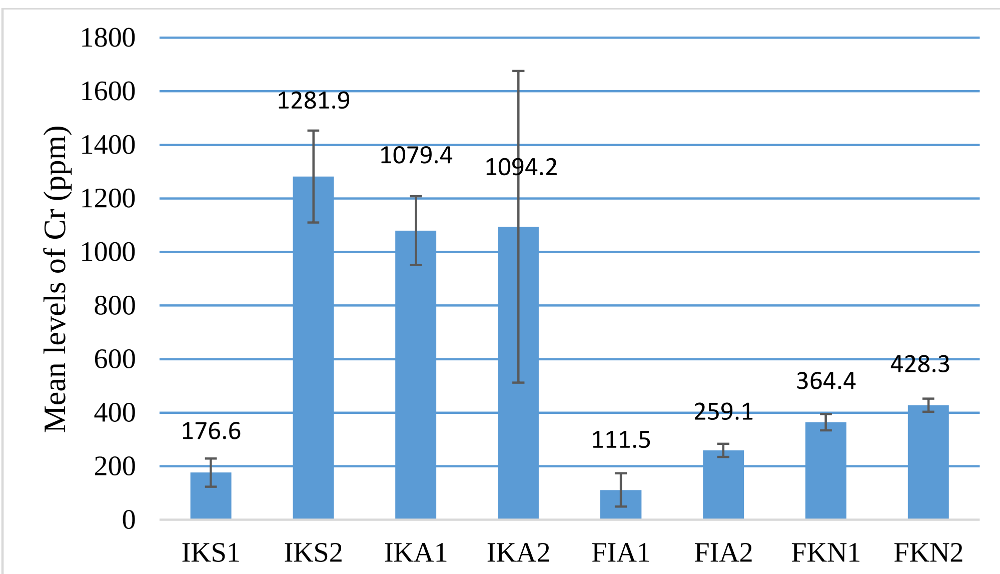


Figure 4. 5: Comparison of chromium levels (ppm) in paints procured from different informal and formal retail shops

From Figure 4.5 it was observed that the paint samples from the Informal Kariobangi South, shop 2 (IKS2) samples had the highest chromium levels (1281.87±171.8 ppm) while shop 1

(IKS1) had the lowest levels of chromium (176.61±52.6 ppm). For the formal retail shops from Industrial area paint samples (FIA1, FIA2) had lower levels of chromium compared to those from Kariobangi North area shops (FKN1, FKN2). FIA1 had the lowest chromium levels of 111.5±61.9 ppm and FKN2 had the highest levels of 428.3±24.6 ppm (Figure 4.5). The chromium levels in automotive paints from formal retail shops were significantly different at $P < 0.05$ and 95% confidence level form the anova analysis carried out . The levels of chromium were mostly higher in samples procured from informal retail shops compared to those from formal retail shops. This showed that the pigments used in formulation of paint samples from informal retail shops contained high levels of chromium compounds. For example Chromium (VI) Oxide which is mostly used in paint.

4.2.2 Chromium levels in different colours of automotive paints

The chromium level for each colour (white, red, blue and green) was calculated for paint samples purchased from formal retail shops (FIA1, FIA2, FKN1,FKN2) and informal retail shops (IKS1, IKS2, IKA1, IKA2). Comparison of colours was done as shown in the Figure 4.6.

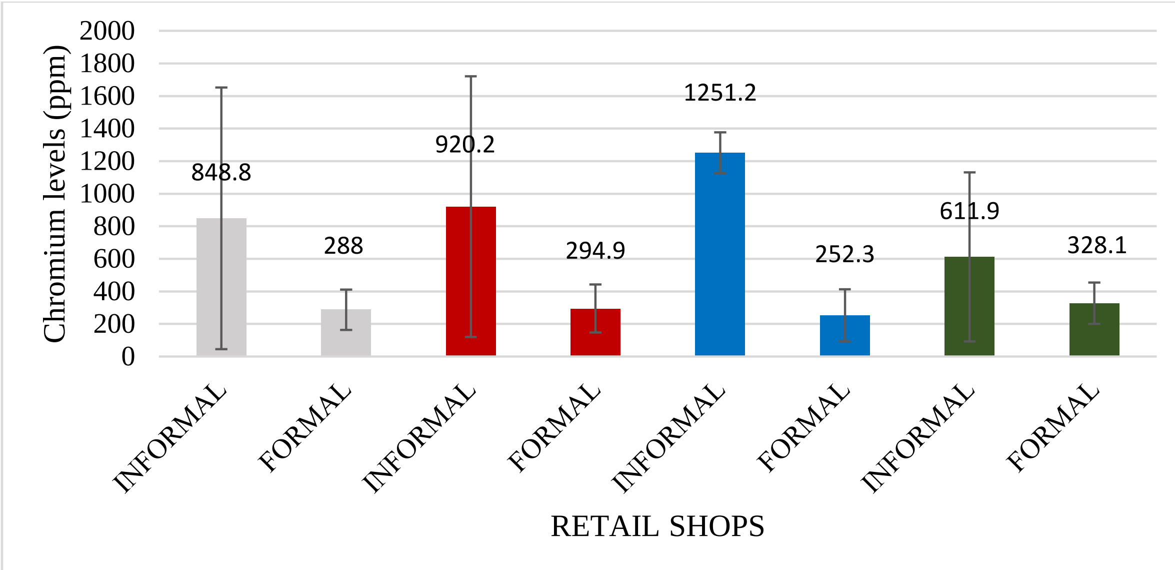


Figure 4. 6: Comparison of chromium levels (ppm) in different colours of automotive paint samples from informal and formal retail shops

From Figure 4.6, it was observed that the paint samples purchased from informal retail shops, the blue colour had the highest chromium levels of 1251.2±125.8 ppm while the green had the lowest (611.9±519.3 ppm). However, automotive paints purchased from formal retail shops, the green colour had the highest levels of chromium of 328.1±126.8 ppm and the blue colour had the lowest (252.3±160.5 ppm). The t-test analysis on chromium levels for the formal and informal retail shops showed that they were statistically different at $p > 0.05$, 95% confidence level. The results showed that chromium compounds are usually used in the manufacture of paint because they exhibit many different colours such as green, blue, red, yellow, orange, black, and other colours. Lead (II) chromate which is also referred to as chrome yellow, chromium (III) oxide (green in colour) is used as a pigment (Verger *et al*., 2018). The use of these compounds in the manufacture of the paints leads to high concentrations of chromium in paint which could have adverse health effects (Lin *et al*., 2019). Paint sprayers are exposed to the metal chromium through the sanding of car paints and vehicle parts. In the short term, chromium VI is known to cause eye, skin, and respiratory irritation as well as gastrointestinal effects that include vomiting and hemorrhage. Chronic exposure to this metal can be incredibly harmful. In the long term, it can bring about harm to the respiratory tract, including limited respiratory function, perforations, and ulcerations of the nasal septum, bronchitis, and pneumonia. It can likewise have adverse consequences for the liver, kidney, and the general immune system (ATSDR, 2012).

4.2.3 Chromium level in paints from formal and informal retail shops

Chromium levels in paint samples purchased from formal and informal retail shops were calculated and compared irrespective of the location and colour of the paints as shown in Figure 4.7.

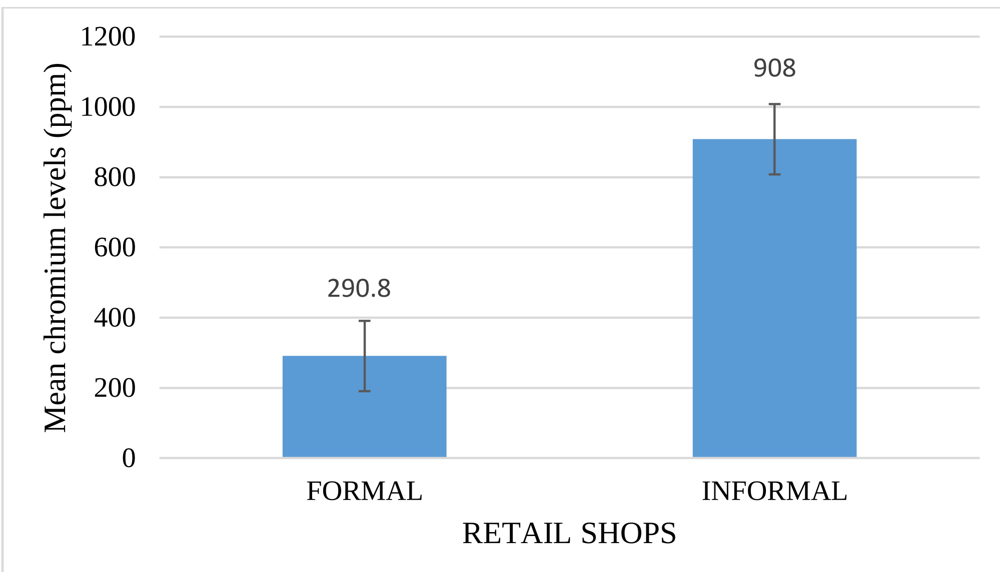


Figure 4. 7: Comparison of chromium levels (ppm) in automotive paints from formal and informal retail shops

Irrespective of the location and colour of paints,the informal retail shops had the highest level of chromium with 908.0±264.0 ppm while formal retail shop paint samples had chromium levels of 290.8±138.4 ppm. At 95% confidence level from t-test analysis, the p value was less than 0.05

showing a similar trend as that of lead levels. The results showed that the paint samples from informal retail shops are far from complying with the existing standards as they are still using raw materials containing chromium compounds in higher percentage resulting to high levels of chromium. It is also difficult for formal paint manufacurers to adhere to the standard when the raw materials containing heavy metals are readily available on the market.

4.3 Cadmium levels in automotive paints

Cadmium levels for each paint sample purchased from informal retail shops (IKS1, IKS2, IKA1, IKA2) and formal retail shops (FIA1, FIA2, FKN1 and FKN2 are presented in Table 4.3. The maximum allowed cadmium in paint according to European Union is 100 ppm (Table 4.3).

Table 4. 3: Levels of cadmium (ppm) in paint samples of different colours from informal and formal retail shops.

Sampled sites			Mean levels of cadmium (ppm) in various colours of automotive paints				Mean	Maximum Allowed Limit of Cd in paint (ppm) (EU, 2016)
			White	Blue	Red	Green		
Informal Retail Shops	Kariobangi South	IKS1	4.2±1.8	2.4 ±1.5	4.3±2.8	2.5±1.8	3.4±1.0	100
		IKS2	6.5 ±0.4	3.6±0.0	4.2±0.8	4.8±0.1	4.7±1.2	
	Kamukunji	IKA1	8.3±0.4	6.8±0.3	8.2±0.3	9.8±0.2	8.2±1.2	
		IKA2	11.7±0.5	9.7±0.1	10.3±0.5	12.5±0.6	11.1±1.2	
Mean			7.7±3.2	5.6±3.3	6.8±3.0	7.4±4.6		
Formal Retail Shops	Industrial Area	FIA1	6.1±0.2	5.5±1.0	2.9±0.1	6.0±0.2	5.1±1.5	
		FIA2	10.9±0.1	7.5±0.3	10.1±0.1	11.9±0.1	10.1±1.9	
	Kariobangi North	FKN1	15.8±0.0	13.7±0.5	17.3±0.1	18.0±0.4	16.2±1.9	
		FKN2	23.0±0.6	19.7±0.4	22.4±0.51	24.8±0.1	22.5±2.1	
Mean			14.0±7.2	11.6±6.4	13.2±8.5	15.2±8.0		

All (100%) the samples purchased from both formal and informal retail shops had cadmium levels that fell within the acceptable set limit of 100 ppm (EU, 2016, Table 4.3). For instance, the red colour paint from Informal Kariobangi South Shop 1 (IKS1) had the highest levels of 4.3±2.8 ppm while blue colour from the same shop had the lowest levels of 2.4±1.5 ppm. On the other hand, the white paint from the Informal Kariobangi South Shop 2 (IKS2) had the highest levels of 6.5±0.4 ppm while the blue paint had the lowest level of 3.6±0.0 ppm. Paint samples procured from the Infromal Kamukunji Area Shop 1 (IKA1) reported the highest levels of 9.8±0.2 ppm in green colour while the lowest was 6.8±0.3 ppm in blue colour. The second retail shop (IKA2) the highest concentration of 12.5±0.6 ppm in green colour and 9.7±0.1 ppm in blue colour. In all cases, paint samples procured from the informal retail shops, the blue colours had the lowest Cd levels.

The paints purchased from Formal Industrial Area Shop (FIA1) had the highest levels of Cd in white colour (6.1±0.2 ppm), followed by green (6.0±0.2 ppm), blue (5.5±1.0 ppm), and red colour (2.9±0.1 ppm). Samples from shop 2 (FIA2) had the highest Cd levels in green colour (11.9±0.1 ppm) and lowest in blue colour (7.5±0.3 ppm). Samples from Kariobangi North shop 1 and 2 (FKN1 and FKN2) had the highest and lowest levels of Cd in green and blue colour respectively. The levels were however higher in paint samples from industrial area than the Kariobangi retail shops though they were within the set limit of 100 ppm. Overall, the green colour had the highest Cd levels. The green pigment is due to a mixture of cadmium yellow and chrome green commonly used in formulation of paints and this may be responsible for increased Cd levels.

4.3.1 Cadmium levels in automotive paints sold in informal and formal retail shops

The cadmium levels in each retail shop (formal and informal)are presented in Figure 4.8. The different levels of cadmium in paint samples from informal retail shops (IKS1, IKS2, IKA1 and IKA2) and informal retail shops (FIA1, FIA2, FKN2 and FKN2) were then compared.

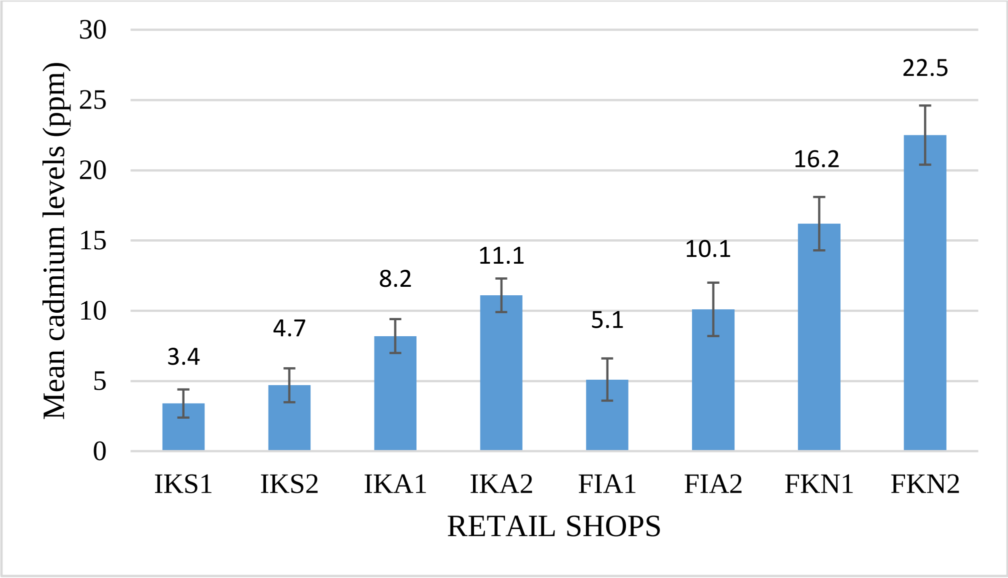


Figure 4. 8: Comparison of cadmium levels (ppm) in paints procured from different informal and formal retail shops

From Figure 4.8, it was observed that Informal Kariobangi South Shops 1 and 2 (IKS1 and IKS2) had lower levels of Cd than those purchased from Infromal Kamukunji Area Shops 1 and 2 (IKA1 and IKA2) although all of the samples were within the set limit of 100 ppm. IKS1 had the lowest of 3.4±1.0 ppm while IKA2 had the highest level of 11.1±1.3 ppm. From ANOVA analysis, the levels of Cd in all the informal retail shops were significantly different ($p < 0.05$). For the formal retail shops' samples from Kariobangi North Shop 2 (FKN2) had the highest Cd levels with a concentration of 22.5±2.1 ppm followed by FKN1 (16.2±1.9) ppm, then FIA2 (10.1±1.9) ppm and FIA1 (5.1±1.5) ppm. The levels of cadmium were higher in paint samples from formal retail shops indicating that cadmium pigments were used in paint formulationdespite them being expensive and scarce while in the informal retail shops low amount of Cd pigments could have been used. These levels were statistically different at $p<0.05$ across the formal shops. Although the levels of Cd were observed to be lower than the set limit, studies have shown that at very low levels Cd compared to other toxic metals can disrupt the functions of the biological systems (Bernard, 2008).

4.3.2 Cadmium levels in different colours of automotive paints

The cadmium levels in formal and informal retail shops were calculated for each colour (white, red, blue and green) irrespective of the location they were purchased from. Comparison of each colour between formal and informal retail shop samples was done and discussed below.

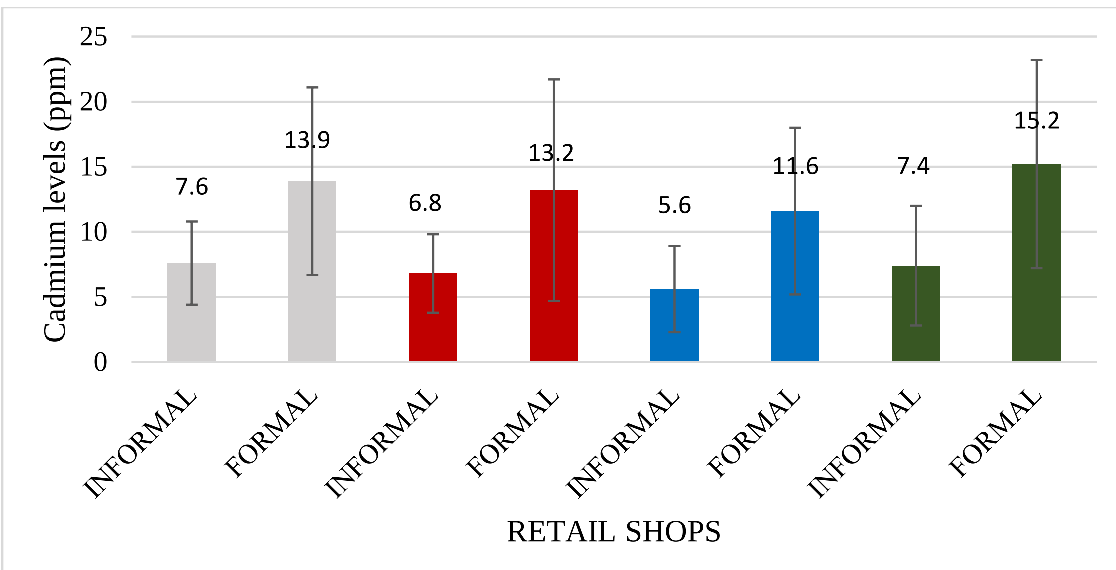


Figure 4. 9: Comparison of cadmium levels (ppm) in different colours of automotive paint samples from informal and formal retail shops.

All the paint colours (white, red, blue, green) from formal retail shops had higher levels of Cd than those from the informal retail shops regardless of their locations. This means that raw materials used during manufacturing of paints in formal sectors contained higher % of Cd compounds. The Cd levels in the four colours from formal and informal retail shops had no significant difference at p>0.05, 95% confidence level. Pigment containing Cd are known for excellent light-fastness and are preferred in paints as they give brilliant colours. For example, Cd-yellow (cadmium sulphide), Cd-orange (cadmium selenide), and Cd-red (cadmium selenide) are some of the bright pigments commonly sold in the markets (Buxbaum and Ptaff, 2005). The higher levels of cadmium in paint samples from formal retail shops could be attributed to use of cadmium selenide in large amount as a pigment giving the paint different shade of colours.

4.3.3 Cadmium level in paints from formal and informal retail shops

Cadmium levels for paint samples purchased from formal retail shops were calculated irrespective of the colour or the location they were obtained from. The same was done for samples purchased from informal retail shops. Comparison of the paint samples between formal and informal retail shops was done.

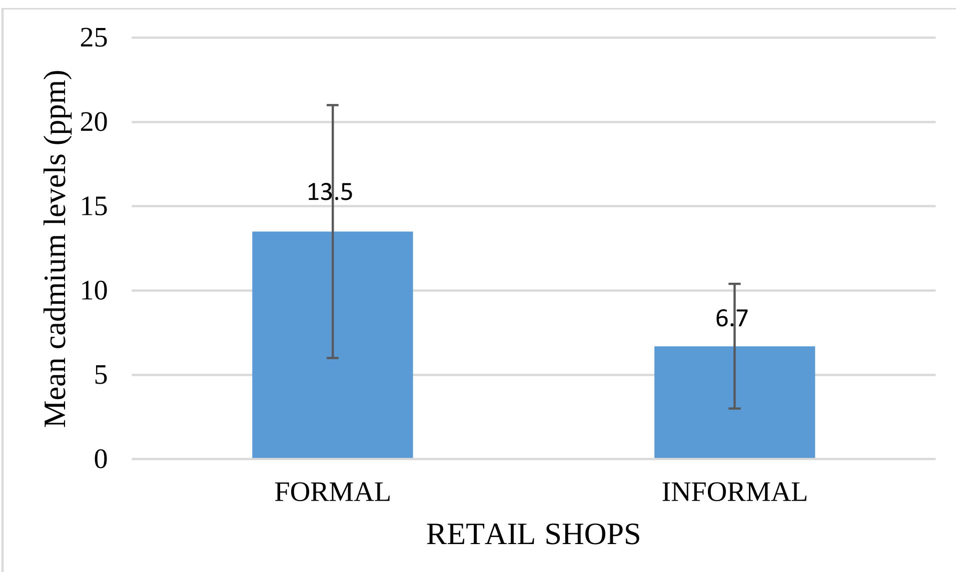


Figure 4. 10: Comparison of cadmium levels (ppm) in automotive paints from the formal and informal retail shops

Formal and informal retail shops paint samples had a mean Cd levels of 13.5±7.5 ppm and 6.7±3.7 ppm respectively (Figure 4.10). Irrespective of location and colour the Cd levels differed significantly at a 95% confidence level ($p<0.05$) from formal and informal retail shops. Cadmium levels in paint samples from formal retail shops were higher than those from informal retail shops unlike for lead and chromium in which the levels were higher in paint samples from informal retail shops. Cadmium pigments are scarce and expensive and thus used in little amount in informal retail shop' paints than in formal retail shop' paints.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

All the thirty two automotive paint samples that were analysed, showed that automotive paints sold in some formal and informal retails shops in Nairobi County, Kenya contained high levels of lead and chromium thereby exposing paint sprayers to high health risks. Among the sixteen paint samples from formal retail shops only one blue paint sample had lead level below the acceptable limit according to the Kenya Bureau of Standards (KEBS) while the rest of the samples exceeded the 90 ppm limit.The levels ranged from 115.6±16.1 to 555.2±36.1 ppm. Lead levels in all of the sixteen paint samples from informal retail shops had lead levels above the set limit with their concentrations ranging from 221.0±1.4 to 2688.4±19.5 ppm (KEBS, 2018).

For chromium, only two samples (94.8±8.1 and 39.3±7.0 ppm) out of sixteen paint samples from formal retail shops, had acceptable levels of chromium that was within the limit of 100 ppm according to the European Union whereas the rest varied from 123.9±0.8 to 461.9±11.1 ppm. For the informal retail shops, all the samples had chromium levels ranging from 120.5±10.6 to 2771.9±35.6 ppm. The high levels of lead and chromium could be attributed to the use of lead driers and pigments in the raw materials during manufacturing of automotive paints.

The study established that paint samples from informal retail shops had significantly high levels of lead and chromium compared to the formal retail shops. Most of the paint samples did not comply with the maximum acceptable limits which means that they were not safe for use by the spray painters. However, cadmium levels in all paint samples from both formal and informal retail shops ranged from 2.4±1.8 to 24.8±0.1 ppm and were within the acceptable limit of 100 ppm according to EU (2016) indicating that cadmium levels in all paint samples complied with the maximum acceptable limit. Despite the different levels of lead, chromium and cadmium observed in the automotive paint samples, their presence in the paints raises health concern among the spray painters due to their accumulation even at low levels.

5.2 Recommendations

The recommendations from this study are:

- The information on the lead levels in the automotive paints be used as the basis of determining lead levels in blood among the spray painters working in the informal garages.
- Assessment of lead, chromium, and cadmium in automotive paints in other colours from other informal and formal retail shops in Nairobi.

REFERENCES

Abdalla, S. M., Salah, M. A. I., Howeida, H. A., Elsadig, Y. M (2016). *World journal of Pharmacy and Pharmaceutical Sciences*, **5**(5), 815-825.

Achmad, R. T. and Auerkari, E. I. (2017). Effects of chromium on human body. *Annual Research & Review in Biology*, pp. 1-8.

Adei, E., Adei, D., Osei-Bonsu, S. (2011). Assessment of perception and knowledge of occupational chemical hazards, in the Kumasi metropolitan spray painting industry, *Journal of Science and Technology*, **31**(2), 83-94.

Ahmad, I., Rehan, M., Balkhyour, M. A., Abbas, M., Basahi, J. M., Almeelbi, T. (2016). Review of environmental pollution and health risks at motor vehicle repair workshops: Challenges and perspectives for Saudi Arabia. *International Journal of Agriculture and Environmental Research*. **2**(1), 1-20.

Ansdell, D. A. (1999). Automotive paints. *Paint and surface coatings: theory and practice*, pp. 431-489.

Awodele, O., Popoola, T. D., Ogbudu, B. S., Akinyede, A., Coker, H. A., Akintonwa, A. (2014). Occupational hazards and safety measures amongst the paint factory workers in Lagos, Nigeria. *Safety and health at work*, **5**(2), 106-111.

Baba, H., Tsuneyama, K., Yazaki, M. (2013). The liver in itai-itai disease (chronic cadmium poisoning) pathological features and metallothionein expression. *Mod Pathol*., **26**:1228-1234.

Baselt, R. C. (2008). Disposition of Toxic Druds and Chemicals in man (8th ed.). Foster City: Biomedical Publications, pp. 305-307.

Basketter, D., Horev, L., Slodovnik, D., Merime, S., Trattner, A., Ingber, A. (2000). Investigation of the threshold for allergic reactivity to chromium. *Contact Dermatitis*, **44**(2), 70-74.

Baur, X., Aasen, T. B., Burge, P. S., Heederik, D., Henneberger, P. K., Maestrelli, P. (2012). ERS Task Force on the Management of Work-related, Asthma. The management of work-related asthma guidelines: a broader perspective. *European Respiratory Review*, **21**(124), 125-139.

Bentley, J. O. H. N. (2001). *Composition, manufacture and use of paint*. Taylor and Francis, Inc.: New York, pp. 123-142.

Bernard, A. (2004). Renal dysfunction induced by cadmium; Biomarkers of critical effects Biometals, **17**:519-523.

Bernard, A. (2008). Cadmium and its adverse effects on human health. *Indian J Med Res.*,**128**(4), 557-64.

Bieleman, J. H. (2000). Ed. in Additives for Coatings, Wiley-VCH, Weinheim, New York,USA, pp. 1-202.

Bishak, Y. K., Payahoo, L., Osatdrahimi, A. (2015). Mechanisms of cadmium carcinogenicity in the gastrointestinal tract. *Asian Pac J Cancer Prev,* **16**(1), 9-21.

Bradshaw, L. M., Fishwick, D., Slater, T., Pearce, N. (1998). Chronic bronchitis, work-related respiratory symptoms, and pulmonary function in welders in New Zealand. *Occup. Med.*, **55**:150-154.

Briggs, D. (2003). Environmental pollution and the global burden of disease. *British medical bulletin*, **68**(1), 1-24.

Brill, T. B. and Falk, D. S. (1981). Light: Its interaction with art and antiquities. *American Journal of Physics*, **49**(5), 510-510.

Brokbartold, M., Wischermann, M., Marschner, B. (2012). Plant availability and uptake of lead, zinc, and cadmium in soils contaminated with anti-corrosion paint from pylons in comparison to heavy metal contaminated urban soils. *Water Air Soil Pollut*., **223**:199-213.

Brown, L.M., Moradi, T., Gridley, G., Plato, N., Dosemeci, M., Fraumeni, J.F. Jr. (2002). Exposures in the painting trades and paint manufacturing industry and risk of cancer among men and women in Sweden. *J. Occup. Environ. Med.*, **44**:258-264.

Buxbaum, G. and Pfaff, G. (2005). Cadmium Pigments. Industrial inorganic pigments. Wiley-VCH, pp. 121-123.

Buxbaum, G. (2008). *Industrial inorganic pigments*. John Wiley & Sons, pp. 105-206.

Chan-Yeung, M. and Malo, J. L. (1994). Aetiological agents in occupational asthma. *Eur Respir J.*, **7**:346-371.

Chowdhury, R., Sarnat, S. E., Darrow, L, McClellan, W, Steenland, K. (2014). Mortality among participants in a lead surveillance program. *Environmental Research*, **132**:100-104.

Costa, M. and Klein, C. B.(2006). Toxicity and carcinogenicity of chromium compounds in humans. *Crit Rev Toxicol,* **36**:155-163.

Dapul, H. and Laraque, D. (2014). Lead poisoning in children. *Advances in paediatrics,* **61**(1), 313-333.

Enander, R. T., Gute, D. M., Cohen, H. J., Brown, L. C., Desmaris, A. M. C., Missaghian, R. (2002). Chemical characterization of sanding dust and methylene chloride usage in automotive refinishing: implications for occupational and environmental health. *AIHA Journal*, **63**(6), 741-749.

Fettis, G. (2008). *Automotive paints and coatings*. John Wiley & Sons, pp. 28-29.

Flora, S. J., Flora, G., Saxena, G. (2006). Environmental occurrence, health effects and management of lead poisoning. In *Lead*, pp. 158-228.

Freitag, W. and Stoye, D.(2008). *Paints, coatings and solvents*. John Wiley & Sons, pp. 3-7.

Gaitens, J.M., Dixon, S. L., Jacobs, D. E., Nagaraja, J., Strauss, W., Wilson, J. W., Ashley, P. (2008). U.S. Children's Exposure to Residential dust lead, 1999-2004: Housing and Demographic Factors. *Environmental Health Perspectives*, **117**(3), 461-467.

García, R., and Báez, A. P. (2012). Atomic absorption spectrometry (AAS). *Atomic absorption spectroscopy*, **1**:1-13.

Gidlow, D. A. (2015). Lead toxicity, *Occupational Medicine*, **65**(5), 348-356.

Goyer, R. A. (2001). Toxic effects of metals. In: Klaassen CD, editor. Cassarett and Doull's Toxicology: The Basic Science of Poisons. New York: McGraw-Hill Publisher, pp. 811-867.

Guertin, J. (2005). Toxicity and health effects of chromium (all oxidation states) In: Guertin J, Jacobs JA, Avakian CP, editors. Chromium (VI) Handbook. Boca Raton, FL: CRC Press, pp. 1-22.

Guha, N., Steenland, K., Merletti, F., Altieri, A., Cogliano, V., Straif, K. (2010). Bladder cancer risk in painters: A meta-analysis. *Occup. Environ. Med.*, **67**:568-573.

Hansen, M. B., Johansen, J. D., Menné, T. (2003). Chromium allergy: significance of both Cr (III) and Cr(VI). *Contact Dermatitis*, **49**(4), 206-212.

Hayes, A. W. (2007). Principles and Methods of Toxicology. Philadelphia: CRC Press, pp. 858-861.

Higgitt, C., Spring, M., Saunders, D. (2003). Pigment-medium interactions in oil paint films containing red lead or lead-tin yellow. *National Gallery Technical Bulletin*, **24**:75-95.

International Agency for Research on Cancer (IARC) (2010). Painting, firefighting and shiftwork. Monogr *Eval Carcinog Risks Hum*., **98**:1-804.

International Agency for Research on Cancer (IARC) (2004). Inorganic and organic lead compounds: Inorganic lead compounds (Group 2A), Organic lead compounds (Group 3). *International Agency for Research on Cancer*, **87**:403-413.

International Lead and Zinc Study Group (ILSG) (2004). World lead chemicals productions and usage. Lisbon, Geneva, pp. 216-234.

Ishola, A. B., Okechukwu, I. M., Ashimedua, U. G., Uchechukwu, D., Michael, E. A., Moses, O. O., Ifeanyichukwu, O. K. (2017). Serum level of lead, zinc, cadmium, copper and chromium among occupationally exposed automotive workers in Benin city. *Int J Environ Pollut Res.*, **5**(1), 70-79.

Jacobs, J. A. and Testa, S. M. (2005). *Overview of chromium (VI) in the environment: background and history*. In: Guertin J, Jacobs JA, Avakian CP, editors. Chromium (VI) Handbook. Boca Raton, Fl: CRC Press, pp. 1-22.

Jaishankar, M., Tseten, T., Anbalagan, N., Mathew, B. B., Beeregowda, K. N. (2014). Toxicity mechanism and health effects of some heavy metals. *Interdisciplinary toxicology*, **7**(2), 60-72.

Kameti, C. M. (2003). Determination of lead and cadmium in decorative paints in Nairobi, Kenya. MSc Thesis, Kenyatta University.

Karri, S. K., Sapper, R. B., Kales, S. N. (2008). Lead Encephalopathy Due to Traditional Medicines. *Current Drug Safety*, **3**(1), 54-59.

Kaukiainen, A., Riala, R., Martikainen, R., Estlander, T., Susitaival, P., Aalto-Korte, K. (2005). Chemical exposure and symptoms of hand dermatitis in construction painters. *Contact Dermatitis*, **53**:14-21.

Keski-Säntti, P., Kaukiainen, A., Hyvärinen, H. K., Sainio, M. (2010). Occupational chronic solvent encephalopathy in Finland 1995–2007. Incidence and exposure. *International Archives of Occupational and Environmental Health*, **83**:703-712.

Lambourne, R. and Strivens, T. A. (Eds.). (1999). *Paint and surface coatings: theory and practice*. Elsevier, pp. 243-283.

Lin, C. H., Lai, C. H., Peng, Y. P., Wu, P. C., Chuang, K. Y., Yen, T. Y., Xiang, Y. K. (2019). Comparative health risk of inhaled exposure to organic solvents, toxic metals, and hexavalent chromium from the use of spray paints in Taiwan. *Environmental Science and Pollution Research*, **26**(33), 33906-33916.

Luevano, J. and Damodaran, C. (2014). A review of molecular events of cadmium-induced carcinogenesis. *J Environ Pathol Toxicol Oncol.*, **33**(3), 183-194.

Marrion, A. (2004). The chemistry and physics of coatings. Royal Society of Chemistry, pp. 287-288.

Mielke, H. W., Powell, E. T., Shah, A., Gonzales, C. R., Mielke, P. W. (2001). Multiple metal contamination from house paints: consequences of power sanding and paint scraping in New Orleans. *Environmental Health Perspectives*, **109**(9), 973-978.

Morrow, H. (2010). Cadmium and Cadmium Alloys. Kirk-Othmer Encyclopedia of Chemical Technology. John Wiley & Sons, pp. 1-36.

Mwatu, A. K. (2011) Health Hazards Associated with Spray Painting Among Workers In Small Scale Auto Garages In Embakasi Division, Nairobi, Kenya. Msc Thesis, School of Health Sciences, Kenyatta University.

Nawrot, T., Plusquin M., Hogervorst J., Roels H. A., Celis H., Thijs L., Vangronsveld J., Van Hecke E., Staessen J. A. (2006). Risk of cancer and environmental exposure to cadmium: a prospective population study. *Lancet Oncol*.,**7**:119-126.

Nduka, J. K., Kelle, H. I., Amuka, J. O. (2019). Health risk assessment of cadmium, chromium and nickel from car paint dust from used automobiles at auto-panel workshops in Nigeria. *Toxicology reports*, **6:**449-456.

Needleman, H. (2004). Lead poisoning. *Annual Review of Medicine*, **55**:209-222.

Nijhawan, R. I., Molenda, M., Zirwas, M. J., Jacob, S. E. (2009). Systemic contact dermatitis. *Dermatologic Clinics*, **27**(3), 355-364.

NIOSH (1978). National Institute for Occupational Safety and Health. U.S. Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, Criteria for a Recommended Standard: Occupational Exposure to Inorganic Lead, Revised Criteria. DHEW (NIOSH), pp. 78-158.

Ogilo, J. K., Onditi, A. O., Salim, A. M., Yusuf, A. O. (2017). Assessment of levels of heavy metals in paints from interior walls and indoor dust from residential houses in Nairobi City County, Kenya. *Chemical Science International Journal*, **21**(1), 1-7

Otero, V., Campos, M.F., Pinto, J.V., Vilarigues, M., Carlyle, L., Melo, M. J. (2017). Barium, zinc and strontium yellows in late 19th–early 20th century oil paintings. *Herit Sci*., **5**(1), 1-13.

Pearce, J. M. (2007). Burton's line in lead poisoning. *European neurology***,** **57**(2), 118-119.

Ragan, P. and Turner, T. (2009). Working to prevent lead poisoning in children getting the lead out. JAAPA, **22**(7), 40-45.

Raymond, J. and Brown, M. J. (2016). Blood Lead Levels in Children Aged <5 Years — United States, 2007–2013. MMWR *Morb Mortal Wkly Rep*., **63**:66-72.

Reisch, M. S. (2003). Paints & coatings. *Chemical & engineering news,* **81**(44), 23-23.

Schutte, R., Nawrot, T.S., Richart, T., Thijs, L., Vanderschueren, D., Kuznetsova, T. (2008). Bone resorption and environmental exposure to cadmium in women: a population study. *Environ Health Perspect***,** **116**:777–783.

Selevan, S. G., Rice, D. C., Hogan, K. A., Euling, S. Y., Pfahles-Hutchens, A., Bethel, J. (2003). Blood lead concentration and delayed puberty in girls. *N Engl J Med.*, **348**(16), 1527-1536.

Streitberger, H. J. and Dossel, K. F. (2008). Automotive Paints and Coatings,Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, pp. 129-174

Tarlo, S. M. and Lemiere, C. (2014). Occupational asthma. *The New England Journal of Medicine*, **370**(7), 640-649.

Tchounwou, P. B., Yedjou, C. G., Patlolla, A. K., Sutton, D. J. (2012). Heavy metal toxicity and the environment. In: Luch A, editor. Molecular, clinical and environmental toxicology. Basel: Springer, pp. 133–164.

Tse, L. A., Yu, I.T.S., Au, J.S.K., Qiu, H., Wang, X.R. (2011). Silica dust, diesel exhaust, and painting work are the significant occupational risk factors for lung cancer in nonsmoking Chinese men. *British Journal of Cancer*, **104**:208-213.

Turner, G.P. (1980). Introduction to Paint Chemistry and Principles Paint Technology: 2nd Ed. London-New York, Chapman and Hall, pp. 108-134.

Verger, L., Dargaud, O., Chassé, M., Trcera, N., Rousse, G., Cormier, L. (2018). Synthesis, properties and uses of chromium-based pigments from the Manufacture de Sèvres. *Journal of Cultural Heritage*, **30:**26-33.

Vitayavirasuk, B., Junhom, S., Tantis-baeranee, P. (2005). Exposure to lead, cadmium and chromium among spray painters in automobile body repair shops. *J. Occup. Health*, **47**:518-522.

Vos, T., Flaxman, A. D., Naghavi, L. R., Michaud, C., Ezzati M. (2010). A systematic analysis for the Global Burden of Disease Study Lancet, **380**:2163-2196.

Wise, S. S. and Wise, J. P. Sr. (2012). Chromium and genomic stability. *Mutation Research/Fundamental and Molecular Mechanisms of Mutagenesis*, **733**(1–2), 78–82.

Woolf, A.D., Goldman, R., Bellinger, D.C. (2007). Update on the clinical management of childhood lead poisoning. *Pediatric clinics of North America*, **54**(2), 271-294.

Internet References

ASTM E1282-98 (2004). Standard Guide for Specifying the Chemical Compositions and Selecting Sampling Practices and Quantitative Analysis Methods for Metals, Ores, and Related Materials, ASTM International, West Conshohocken, PA, Retrieved from http:/www.astm.org/cgi-bin/resolver.cgi?E1282.

ATSDR (2008). Agency for Toxic Substances and Disease Registry, U.S. Department of Health and Human Services. Atlanta, GA: Public Health Service; Toxicological Profile for Chromium, Retrieved from http://www.atsdr.cdc.gov/ToxProfiles/TP.asp?id=62&tid=17.

ATSDR (2010). Agency for Toxic Substances and Disease Registry. Toxicological Profile for Lead. Atlanta, GA: Department of Health and Human Services. [updated 2015 Jan. 21; accessed2016Nov.14].Retrievedfrom: https://www.atsdr.cdc.gov/ToxProfiles/tp.asp?id=96&tid=22.

ATSDR (2012). Agency for Toxic Substances and Disease Registry. Toxicological Profile for Cadmium. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service, Retrieved from http:/www.atsdr.cdc.gov/toxfaqs/tf.asp?id=47&tid=15.

CDC (2001). Centers for Disease Control and Prevention Managing Elevated Blood Lead Levels Among Young Children: Recommendations From the Advisory Committee on ChildhoodLeadPoisoningPrevention. AtlantaRetrievedfromhttps:/www.cdc.gov/Mmwr/preview/mmwrhtml/ss5210a1.htm.

CDC. (2013). Lead Information for Workers. Archived from the original on 18 October 2016. Retrieved 14 October 2016, from https://www.cdc.gov/niosh/topics/lead/workerinfo.html.

EU (2016). Specifies restriction limit for cadmium in certain paints [Internet]. Geneva, Switzerland: SGS; 2016 Feb 25 [cited 2016 Jul 23]. Retrieved from: http://www.sgs.com/en/ news/2016/02/safeguards-04316-eu-specifies-restrictionlimit-for cadmium-in-certain-paints-under-reach.

GAELP (2011). Global Alliance to Eliminate Lead Paint. Retrieved 8.08.2013, from http://www.unep.org/hazardoussubstances/LeadCadmium/PrioritiesforAction/GAELP/GAELPObjectives/tabid/6331/Default.aspx.

ISO 6503:1984. Paints and varnishes - Determination of Total Lead - Flame Atomic Absorption Spectrometric Method (available in English and French) Retrieved from http://www.iso.org/iso/iso_catalogue/catalogue_tc/catalogue_detail.htm?csnumber =12880, accessed 25 July 2017.

KEBS (2018). Kenya gazettes new paint standards to eliminate lead paints (14 February 2018). Retrieved from http://www.ecogreennews.com/kenya-gazettes-new-paint-standards-to-eliminate-lead-paints/

WHO (2010). World Health Organization. Exposure to lead: A major public health concern. Geneva. Retrieved from https://www.who.int/ipcs/features/lead..pdf?ua=1.

WHO (2016). Lead poisoning and health. Archived from the original on 18 October, Retrieved from https:www.who.int/news-room/fact-sheets/detail/lead-poisoning-and-health.

APPENDICES

Appendix 1 : Spray painting in informal (Jua kali) garage

Appendix 2: Digestion of samples on a hot plate

Appendix 3: Questionnaire

The purpose of this questionnaire is to collect information on mostly used automotive paints and colours by the spray painters working in informal garages. This is part of Master of Science degree course in Analytical Chemistry at University of Nairobi. Am requestion you to fill this questionnaire.

Section A: Demographic Information

1. Sex …………….
2. Age ……………..
3. Level of education …………………

Section B: Employment Information

1. Duration in current employment …………………..
2. Main work activity …………………………….

Section C: Paint Used

1. Source of paint used …………………………..
2. Mostly used colours ……………………………..

Appendix 4 : Preparation of working standards

Stock solution – 1000 mg/l in 0.5M Nitric acid

A 100 ppm was prepared in a 50 ml flask from the stock solution of 1000 ppm using C1V1= C2V2 dilution formula

1000 ppm * X ml = 100 ppm * 50 ml

X = 5000/1000

X = 5 ml

5 ml of the stock solution was diluted to 50 ml using distilled water to prepare 100 ppm standard.

The series working standard were prepared from the 100 ppm.

Example: 2 ppm lead (Pb) standard

C1V1 = C2V2

100 ppm * X = 2 ppm * 50 ml

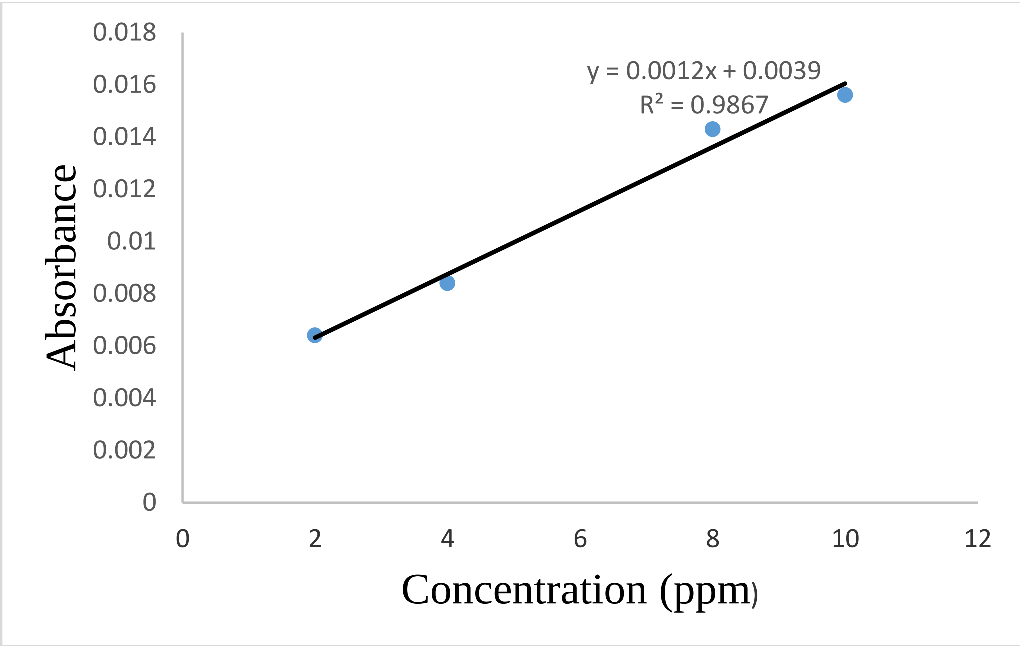
X = 100/100

X = 1 ml

1 ml of the 100 ppm standard was diluted to 50 ml using distilled water to prepare the 2 ppm lead standard.

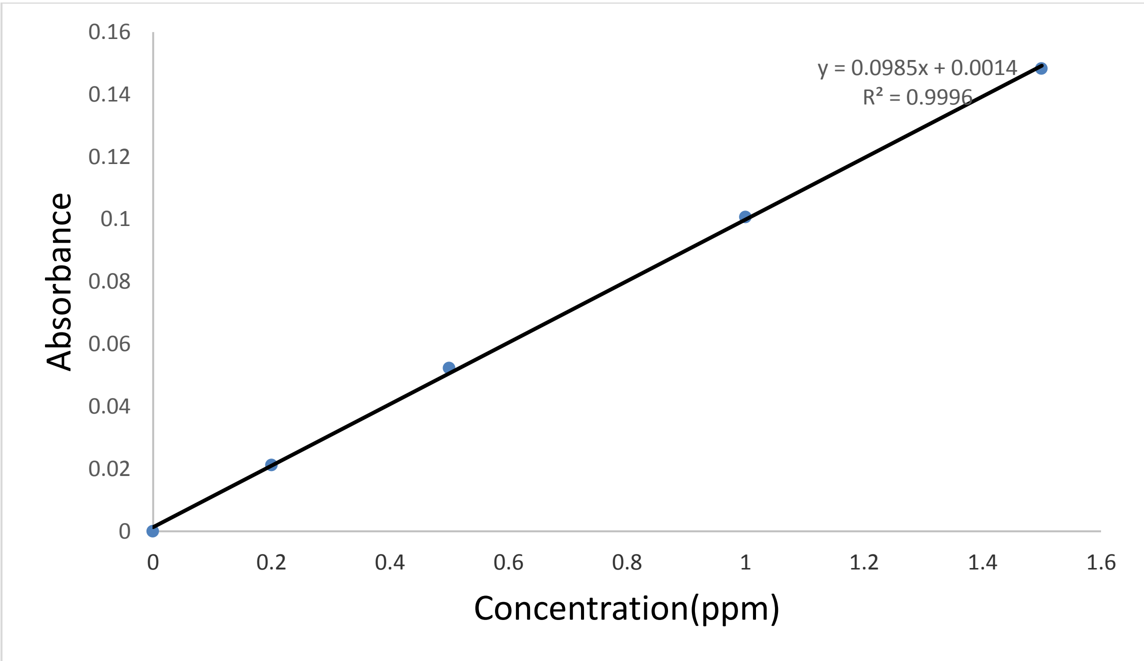
Appendix 5: Calibration curve for lead

Absorbance vs concentration

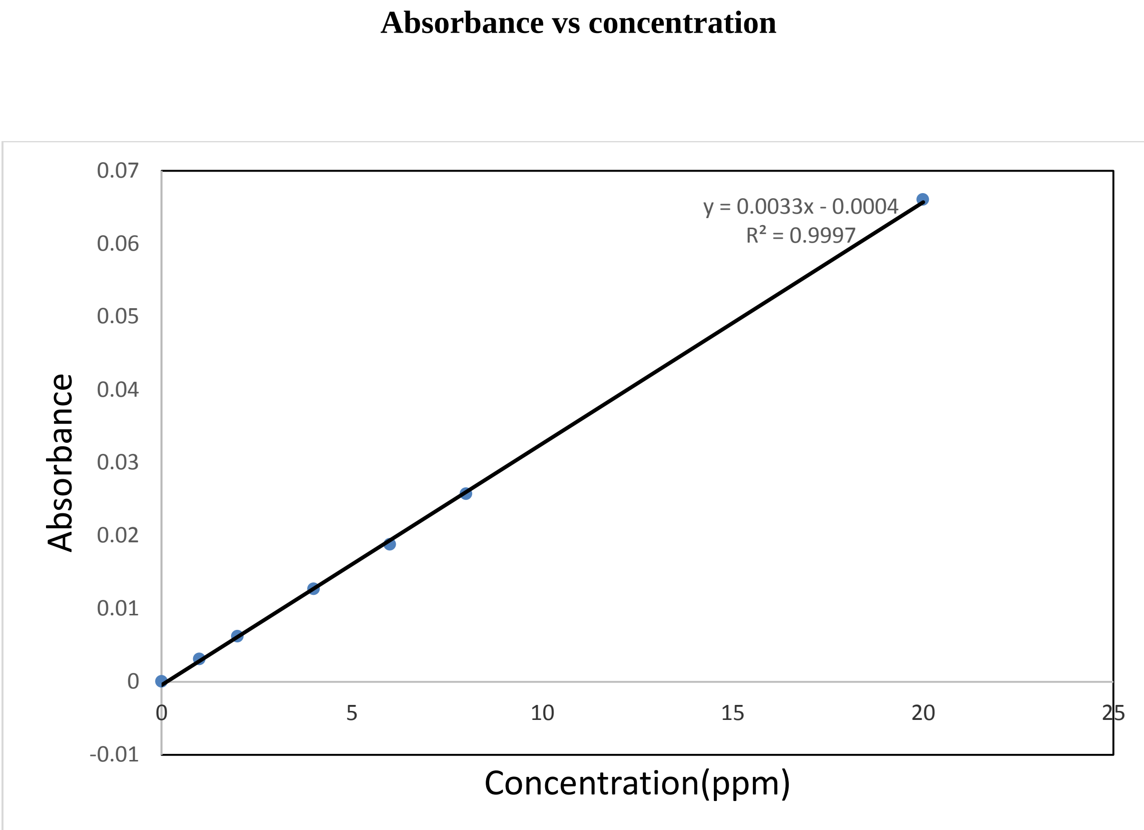


Appendix 6: Calibration curve for cadmium

Absorbance vs concentration



Appendix 7: Calibration curve for chromium



Appendix 8: Sample analysis using AAS

Appendix 9: Formula for calculation of levels (ppm) of each heavy metal in automotive paint samples.

Actual concentration (ppm) of the metal in the sample = Calculating factor * AAS result (ppm)

Where:

Calculating factor = Final volume (ml)/sample weight (g)

<u>Example</u>

Calculation of the lead concentration (ppm) for FIA1 (from industrial area 1) sample in duplicate

Sample 1: AAS result - 0.443 ppm, weight -0.5224 g, final volume -100 ml

Calculating factor = 100/0.5224

=191.424196

Concentration = 0.443 * 191.424196

=84.80091884 ppm

Sample 2 : AAS result - 0.443 ppm, weight – 0.5419 g, final volume – 100ml

Calculating factor =100/0.5419

=184.5358922

Concentration = 0.443 * 184.5358922

=81.74940026 ppm

Average for sample 1 and sample 2 = (84.80091884+81.74940026)/2

=83.27515955 ppm

Appendix 10: Cost of automotive paints from formal and informal retail shops

Retail shop	Quantity	Cost
Formal retail shop	250 ml	Ksh. 300
Informal retail shop	100 ml	Ksh. 100