AKENTEN APPIAH-MENKA UNIVERSITY OF SKILLS TRAINING AND ENTREPRENUERIAL DEVELOPMENT.

HEAVY METAL(LOID)S AND VOLATILE ORGANIC COMPOUNDS IN LOCAL AND IMPORTED COSMETICS PURCHASED FROM KEJETIA MARKET, GHANA AND THEIR HEALTH RISK ASSESSMENT

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MASTER OF PHILOSOPHY

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DECLARATION

I, ………………………………… declare that this thesis, with the exception of quotations and references contained in published works which have all been identified and duly acknowledged, is entirely my own original work, and it has not been submitted, either in part or whole, for another degree elsewhere.

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We hereby declare that the preparation and presentation of this work was supervised in accordance with the guidelines for supervision of thesis as laid down by the Akenten Appiah-Menka University of Skill Training and Entrepreneurial Development.

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Abstract

There is a growing trend of people becoming beauty conscious which exacerbate the health hazards pose on consumers due to heavy metals contamination of cosmetics. This study determined the levels of heavy metal(loid)s and volatile organic compounds (VOCs) in local and imported cosmetics purchased from Kejetia Market and their health risk assessment. Seven (7) metals were analyzed in 21 cosmetic samples. The seven metals assessed include Pb, Cd, As, Fe, Ni, Cr, and Hg. The concentrations of some of the metals in imported cosmetic samples were higher than those found in local cosmetic samples. However, there was no significant difference between the concentrations of the metals in both local and imported cosmetic samples. Also, the Margin of Safety (MoS) values for all the metals in the cosmetics sample were below the World Health Organization (WHO) standard of 100. This implies both local and imported cosmetics samples were not safe and therefore can pose adverse health risks to consumers. The hazard quotient (HQ) and hazard indices (HI) for almost all the metals in the cosmetic samples were greater than their permissible limits, interpreting that there is a health risk associated with the cosmetic samples. On the other hand, carcinogenic risk for Cr and As in local and imported cream and lotion were all higher than the tolerance levels, which implies there is higher possibility of getting cancer when one uses such cosmetic products. Moreover, the concentrations of some of the metals that the regulatory bodies have set a threshold for were observed to be higher than the acceptable permissible limits. Furthermore, the analysis of the cosmetics samples showed that 9 different VOCs are present in the samples. The local samples have VOCs including heptadecanoic acid, pentadecanoic acid, 5, 8, 11, 14-eicosatetraenoic acid, Tridecanoic acid and 9-octadecanoic acid. Whereas, the imported cosmetic samples have VOCs such as undecanoic acid, sterate acid, heptadecanoic acid, cis-11, 14-eicosadienoic acid, and

pentadecanoic acid. In conclusion, all the cosmetics products contain significant levels of the heavy metal(loid)s.

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GLOSSARY OF ABBREVIATIONS

AAS: Atomic Absorption Spectroscopy

AFS: Atomic Fluorescence Spectroscopy

CR: Carcinogenic Risk

CV AFS: Cold Vapour Atomic Fluorescence Spectroscopy

EDTA: Ethylenediaminetetraacetic acid

ETAAS: Electro-Thermal Atomic Absorption Spectroscopy

EU: European Union

FDA: Food and Drugs Authority

GFAAS: Graphite flame Atomic Absorption Spectroscopy

GSA: Ghana Standard Authority

GC: Gas Chromatography

GC-MS: Gas Chromatography – Mass Spectroscopy

HGAAS: Hydride Generation Atomic Absorption Spectroscopy

HI: Hazard Index

HQ: Hazard Quotient

HNO_3: Trioxonitrate (v) acid

H_2O_2: Hydrogen Peroxide

ICP-MS: Inductively Coupled Plasma-Mass Spectroscopy

ICP-OES: Inductively Coupled Plasma-Optical Emission Spectroscopy

LOQ: Level of Quantification

LOD: Level of Detection

MF: Modifying Factor

MoS: Margin of Safety

NOAEL: No Observable Adverse Effect Level

NIST: National Institute of Standards and Technology

RFD: Reference Dose

SED: Systemic Exposure Dosage

SF: Slope Factor

SPSS: Statistical Package for Social Science

UF: Uncertain Factor

USFDA: United States Food and Drugs Authority

USEPA: United States Environmental Authority

UV: Ultraviolet

VOCs: Volatile Organic Compounds

WACOMP: West Africa Competitiveness Programme

WHO: World Health Organization

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background of the study

Globally, the use of cosmetics has seen an upsurge in North America, Europe, Asia, and Africa. The global cosmetic industry was estimated to be $40 billion in 2012 (Owusu-Agyei et al., 2020) and the African cosmetics sector in the same year was worth $ 6.93 billion (WACOMP, 2019). According to Ghana Food and Drugs Authority (FDA), a cosmetic is a substance or mixture of substances manufactured, sold, or represented for use in cleansing, improving, or changing the complexion, skin, hair, eyes, or teeth and involves deodorant and perfumes (Ghana FDA, 2013). People who trade in cosmetics have grouped them into five classes and these include skincare, hair care, colour (make-up), fragrances, and toiletries/others. Cosmetics consist of chemical groups such as heavy metals, parabens, benzyl alcohol, formaldehyde and silica. Among these chemical groups, heavy metal poses a wide variety of health hazards to humans and hence their presence in cosmetics is major public health and environmental concern (Ikehata et al., 2014).

The toxicological effects of heavy metals vary from acute to chronic depending on the route of exposure, receptor sensitivity, metal type, and the metal concentration in cosmetics (Tawila et al., 2019). The toxicity of heavy metals to humans and the environment has been a long-standing issue for years (Ikehata et al., 2014). The recent surge in the use of cosmetics by all groups of people has raised the public health risks due to metals such as Cd, Pb, As, and Hg in cosmetic products. The characteristics of heavy metals including toxicity, non-biodegradable, and bioaccumulation in the human body through inhalation and dermal contact have made heavy metals contamination a serious health concern (karimain et al., 2021). The accumulation rate of metals is higher than the removal rate from body, thereby making it possible for these metals to accumulate in tissues and other organs to exert their toxic effects (Yahya et al., 2021). Despite the significant role of the skin in preventing the body against extraneous pollutants, heavy metals in cosmetics can penetrate the skin since cosmetics are applied directly to the skin thereby causing adverse health effects (Usman et al., 2021). For example, adverse reactions such as cancer, mutations, allergic reaction, respiratory problems, and development problems occur due to heavy metal contamination (Ageel et al., 2022). Ingestion and inhalation were considered the major routes of human exposure to heavy metals until recent studies have unveiled possible higher exposure via dermal contact (Ageel et al., 2022).

Critical evaluation of existing literature revealed that myriad cosmetic types including lipstick, body cream, foundations, and eyeliners are reported to contain significant levels of heavy metals such as Pb, Cd, As, Cr, Ni, and Fe (Mustafa and Shaaban, 2018). In spite of the regulations kept in place to guide their usage in cosmetics. Some heavy metals are utilized in the cosmetics industry as starting materials for manufacturing cosmetics, and these metals even at trace levels can stimulate adverse reactions in the body of humans (Nayak et al., 2021). For instance, chromium hydroxide ($Cr(OH)_3$) and lead acetate ($Pb(C_2H_3O_2)_2$) are used as coloring agents during the production of lipstick and eye shadow (Nayak et al., 2021). Besides, heavy metals present in cosmetics may come from metallic devices used during the manufacturing process or through metallic containers used in packaging these cosmetics products (Zakaria and Ho, 2015).

Reports of adverse consequences as a result of heavy metal contamination of cosmetics keep increasing daily due to high patronage of cosmetic products, especially among women since they now pay more attention to their appearances than ever before (Alam et al., 2019). Cosmetics products that stay on mucus membranes, such as lipstick and eye shadow are deemed to be hazardous since the chemicals in the cosmetics can easily be ingested (Alam et al., 2019). In recent years, the emergence of heavy metals contamination of personal care products (PCP) has attracted a lot of attention worldwide as a result of the health implications they pose to the consumer (Adepoju-Bello et al., 2012). Evidence of extensive heavy metal contamination of cosmetics has given rise to policy formulation to regulate the level of heavy metals in cosmetics, especially the most toxic metals. For example, US FDA has set the maximum threshold for mercury and arsenic in cosmetics to be 1.0 ppm and 3.0 ppm respectively (Borowska and Brzóska, 2015).

Furthermore, volatile organic compounds (VOCs) are also known hazardous compounds that are found in cosmetics. VOCs are organic compounds that are prone to be volatile at room temperature and they include alkanes, alkenes, aromatics, alcohols, aldehydes, ketones, and carboxylic acids (Nurmatov et al., 2013). VOCs are used as ingredients in the manufacturing of household products such as paints, cosmetics, pharmaceuticals, disinfectants, and pesticides (Nurmatov et al., 2013). Many VOCs pose short and long-term adverse health effects to humans even at low levels (Nurmatov et al., 2013).

The Ghanaian cosmetic and personal care products industry is expected to become the number one leading sector which will contribute significantly to the Ghanaian economy in the coming years (WACOMP, 2019). Some of the leading local brands of cosmetics in the Ghanaian market are cocoa care, cocoa expects, Kakam, Habiba, and Hudu. However, a survey conducted on imported lipsticks by Nkansah et al, (2018) revealed that the lipstick samples originated from countries such as India, the USA, China, South Korea, South Africa, and Malaysia. Although the Ghanaian markets have locally-made cosmetics and personal care products, most Ghanaians still prefer imported cosmetics to locally made ones because they see the locally made ones as being substandard. This has created a situation such that most cosmetics shops are dominated by imported cosmetic products. In Ghana, there is very little attention given to exposure to heavy metals and VOCs due to cosmetic usage among the Ghanaian population, as compared to heavy metal exposure via sources such as water, food, and soil (Amartey et al., 2011).

1.2 Problem statement

The high patronage of cosmetics products among all manner of people, including old, young, rich and poor in society has made the cosmetics business booming. In Ghana, there is always a rush for cosmetics products, especially during festive seasons, when parties, weddings, and other activities are organized. Recently, young people especially women pay more attention to their appearance when they are stepping out of their houses. In a survey carried out in the Kumasi Metropolis, with a total of 331 participants, 40.4% have in the past or currently use skin-whitening cosmetics products (Owusu-Agyei et al., 2020). Cosmetics are purposely applied to the body to beautify the physical appearance of an individual. A survey carried out by Ackah et al, (2015) on the level of heavy metals in nail polish and lipstick sold at major markets in Accra reported that all the 20 samples for both nail polish and lipstick contain varying levels of heavy metals (Ackah et al., 2015). Nkansah et al. (2018) also reported significant levels of cadmium and lead in lipstick samples sold in shopping malls in Kumasi Metropolis. Several studies have already been carried out to measure the level of heavy metals in cosmetics in other places such as Nigeria (Akpe et al., 2020), Iran (Azeez et al., 2013), and Bangladesh (Alam et al., 2019).

However, heavy metals and VOCs contamination of cosmetics is becoming a major health concern, and therefore it is becoming an interesting area for research. There is little information about heavy metal contaminations of cosmetics in the Ashanti region. Very few studies have been carried out to evaluate the health risk assessment of heavy metals in cosmetics in Kumasi metropolis. In addition, few attempts have also been made to determine the level of VOCs in cosmetics in the Kumasi metropolis as well as the larger Ghanaian community.

1.3 Justification

There has been an increase in the use of cosmetics in Ghana (Owusu-Agyei et al., 2020). The concerns raised with regard to the use of these products are their safety. Furthermore, the points of application of cosmetic products provides pathway of entry into the human body, where they can reach organs to affect them. The repeated use of cosmetics can lead to bioaccumulation of heavy metals even if they occur at trace levels and that can pose health risks to the user. Also, exposure to VOCs is mainly through inhalation and they can cause adverse health effects including sensory irritation, respiratory symptoms, and even cancer. Therefore, frequent analysis of cosmetic products for their heavy metal and VOCs content will assist regulatory bodies like the Food Drugs Authority (FDA) to set acceptable limits for these metals and VOCs in cosmetics which would help to guarantee the safety of cosmetics. Also, there is a need to create public awareness of the dangers of using both local and imported cosmetics that may contain heavy metals and VOCs. Furthermore, this study will add to the existing knowledge on heavy metal and VOCs contamination of cosmetics.

1.4 Aim

To determine the concentrations of heavy metals and the presence of volatile organic compounds in local and imported cosmetic products in Ghana and assess the health risks the heavy metals pose to the population.

Specific objectives

1. To determine the concentrations of heavy metal(loid)s (Pb, Fe, Cd, As, Ni, Cr, and Hg) in cosmetic products purchased from Kejetia Market, Kumasi.
2. To compare the concentrations of heavy metals in both local and imported cosmetics varieties.
3. To evaluate the health risk posed by the heavy metal(loid)s in the cosmetic samples.
4. To compare the levels of heavy metal(loid)s in cosmetics to international acceptable maximum limits.
5. To conduct a qualitative analysis of volatile organic compounds in both cosmetic samples.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Cosmetics

A cosmetic is defined as any item that is rubbed, poured, sprinkled, or sprayed on, or introduced into or applied to any part of the human body for cleansing, beautifying, promoting attractiveness, or altering the appearance of an individual (Alam et al., 2019). According to Ghana FDA, a cosmetic is a substance or mixture of substances manufactured, sold, or represented for use in cleansing, improving, or changing the complexion, skin, hair, eyes, or teeth and involves deodorant and perfumes (Ghana FDA, 2013). Adepojo-Bello et al. (2012) also explain a cosmetic as any substance or mixture that is intended to be applied on the external parts of the body or placed on the teeth and the mucous membrane of the oral cavity mainly for the reason of cleaning, perfuming, protecting, changing their appearance, correcting body odors, and keeping the surfaces in good condition (Adepojo-Bello et al., 2012).

The use of cosmetics as a routine daily body care product dates back to ancient times (Zainy, 2017). The global cosmetic market has grouped cosmetics into five classes, namely hair care, skincare, color (make-up), fragrance, and toiletries (Loboda and Lopacuik , 2013). There has been high patronage of cosmetic products in countries such as Japan, France, and the US, and this goes to boosts the cosmetic industries in such countries (Mahomoodally and Ramjuttun, 2017). The use of cosmetic products has increased enormously across the globe and in Africa including Ghana. This phenomenon can be a result of the upsurge in the awareness of beautification of the body (Arshad et al., 2020). A survey conducted by Owusu-Agyei et al. (2020) reported that 40% of 334 people use skin whitening products and other cosmetic products in Kumasi Metropolis (Owusu-Agyei et al., 2020).

Cosmetics are mostly made up of natural and synthetic materials in addition to both hydrophilic and hydrophobic substances (Arshad et al., 2020). New cosmetics products are manufactured on daily basis due to an increase in demand for cosmetics coupled with the extension of cutting-edge research and technology in the sector (Loboda and Lopacuik., 2013).

2.1.1 Ingredients in cosmetics

The major ingredients used in manufacturing cosmetics include water, emulsifiers, preservatives, thickeners, emollients, pigments, and fragrances.

2.1.1.1 Water

The water used is distilled water which contains no impurities and is added for the formulation of the cosmetic products.

2.1.1.2 Emulsifiers

The emulsifier provides a uniform medium for the various substances to be able to mix well to enhance an even texture of the cosmetic. Emulsifiers are usually used in creams and lotions. Examples include polysorbate, and potassium cetyl sulfate (Kumar and Tyagi, 2013).

2.1.1.3 Preservatives

They are ingredients added to cosmetics to extend their shelf life and also prevent the growth of microbes in cosmetics. Some of the common preservatives include parabens, salicylic acid, benzyl alcohol, formaldehyde, and tetrasodium EDTA (Carli, 2020).

2.1.1.4 Thickeners

They are agents added to increase the viscosity of the product thereby giving it an appealing consistency. Thickeners are often used in lipsticks, lotions, and other cosmetics. Examples include cetyl alcohol, gelatin, silica, and cetyl palmitate (Carli, 2020).

2.1.1.5 Emollient

Their main role in cosmetics is to prevent water loss, which results in softening of the skin. There are natural and synthetic substances that serve as emollients, including beeswax, olive oil, coconut oil, and petrolatum (Carli, 2020).

2.1.1.6 Coloring agents /pigment

They come in a variety of colors used in cosmetics to change the natural color of a person. Examples include iron oxide, mica flake, manganese, and chromium oxide (Carli, 2020).

2.1.1.7 Fragrance

Most people prefer to use cosmetics with a very nice smell and therefore it is important to select an appealing fragrance during the manufacturing process (Kumar and Tyagi, 2013).

2.1.2 Local cosmetics

The Ghanaian cosmetic and personal care products industry has the potential to become the number one leading sector which will contribute significantly to the Ghanaian economy in the coming years (WACOMP, 2019). Locally produced raw materials in manufacturing cosmetics and personal care products in Ghana include Shea butter, cocoa butter, coconut oil, and black soap (WACOMP, 2019). Many indigenous manufacturers use raw materials such as black soap and Shea butter to produce cosmetics and personal care products for sale locally and for export. Ghanaian cosmetic and personal care products are put into categories. These categories include bathing gels, body creams, body wash, hand creams, body scrubs, and Lip balms. Some of the leading brands of cosmetics and personal care products found on the Ghanaian market include Nivea, Ghandour, Vaseline, Unilever, second image, Dark and lovely, etc. (WACOMP, 2019). The local cosmetics that are common in the market include body lotion, body cream, eyeliners, and lipstick.

2.1.3 Imported cosmetics

Some cosmetics companies in Ghana import their products from countries such as Europe, Cote d'Ivoire, Togo, and Nigeria (WACOMP, 2019). A survey conducted on imported lipsticks by Nkansah et al. (2018) revealed that the lipstick samples originated from countries such as India, the USA, China, South Korea, South Africa, and Malaysia (Nkansah et al., 2018). According to Ackah et al. (2015), the nail polish samples used in their study, out of 14 samples, 5 originated from the USA and only one sample came from China, and the rest had their country of origin not indicated on the container (Ackah et al., 2015). Although the Ghanaian markets have locally-made cosmetics and personal care products, most Ghanaians still prefer imported cosmetics to locally made ones because they see the locally manufactured ones as inferior. This has created a situation such that most cosmetics shops are dominated by imported cosmetic products. The most common imported cosmetic products include body lotion, perfumes, lipsticks, eyeliners, creams, and body powder as well as foundations.

2.2 Heavy metal(loid)s

Heavy metal(loid)s is a term used to describe a group of metal(loid)s that have a higher atomic number (above 20) and a density greater than 5 g/cm^3 (Mishra et al., 2019). These metals include cadmium, lead, mercury, chromium, arsenic, copper, and zinc. Heavy metal(loid)s include both essential and nonessential trace metals which may be toxic to the environment and living organisms based on properties, chemical speciation, and concentration levels (Nollet and De Gelder, 2014). Heavy metal(loid)s cause environmental pollution and biological toxicity problems to humans because they have good inhibitory actions on cells as well as non-biodegradable. Heavy metal(loid)s contamination in the environment is increasing tremendously because of its ubiquitous nature. Humans can be exposed to heavy metals through many sources and these sources include water, food, drugs, and cosmetics (Jan et al., 2015). Generally, heavy metal toxicity in humans occurs when these metals bind with proteins through binding sites which are not made for them and destroy the original metals from their natural binding sites which leads to cell malfunction (Jaishankar et al., 2014).

2.2.1 Lead (Pb)

2.2.1.1 Chemistry

Lead is a bright silvery and slightly bluish metal with an atomic number of 82 and a relative mass of 207. It belongs to group 4 and period 6 on the periodic table and even though lead is a metal, it is a poor conductor of electricity. It exists in two oxidation states, thus +2 and +4 (Pruchnik, 1990). Lead is also malleable, soft, and ductile and because of these properties lead is used to manufacture lead-acid batteries, plumbing materials, and alloys (Jan et al., 2015).

2.2.1.2 Source of Lead

The most common sources of lead exposure are hair dyes, paints, auto exhaust, drinking water, and lead-glazed pottery. Humans are exposed to lead and lead-containing compounds through activities such as the burning of fossil fuels, mining, and jewelry. Pb containing compounds are used as coloring agents to manufacture cosmetics and humans are exposed to lead when they patronized such cosmetic products (WHO, 2010).

2.2.1.3 Toxicity to humans

Lead toxicity occurs when a person ingests a high level of lead. Acute exposure to lead results in loss of appetite, headache, fatigue, arthritis, hypertension, abdominal pains, etc. (Jan et al., 2015). A pregnant woman may experience preterm labour, miscarriages, spontaneous abortion, or give birth to children with low birth weight when exposed to an elevated levels of lead (Jan et al., 2015). Long-term exposure to lead in adults causes decreased nervous system functioning, weakness in fingers, wrist, etc. increase blood pressure, and anemia (Saline and Wendy, 2009). It is reported in literature that lead is toxic even at low levels.

2.2.2 Cadmium (Cd)

2.2.2.1 Chemistry

Cadmium is a silvery-white metal with an atomic number of 48 and a relative mass of 112. It belongs to group 12 and period 5 on the periodic table. It exists in an oxidation state of +2 in most of its compounds. Cadmium has eight isotopes, and some of these isotopes are ^{106}Cd, ^{108}Cd, ^{114}Cd, etc., unlike other metals, cadmium can resist corrosion and is mostly used as a protective coat on other metals (Pruchnik, 1990).

2.2.2.2 Source of cadmium

Sources of cadmium include soil, rocks, coal, cosmetics, cigarette smoke, and mineral fertilizer. Through inhalation and ingestion, humans may get exposed to cadmium and may suffer from acute and chronic intoxication (Jaishankar et al., 2014). Many anthropogenic activities discharge cadmium into the environment which affects living organisms and humans living in it. Cadmium is used in plastics, batteries, and pigments. It is commonly used in electroplating.

2.2.2.3 Toxicity to humans

Cadmium is the most toxic metal, and cadmium and cadmium-containing compounds are known sources of carcinogens to humans (Saline and Wendy, 2009). Excessive exposure to cadmium in humans and animals adversely affects them more by inhalation or ingestion via many sources such as spoiled and wasted food, cigarette, cosmetics, etc. (Mishra et al., 2019). Prolonged exposure to cadmium results in severe health conditions such as kidney damage, prostate dysfunction, bone disease, and cancer (Mishra et al., 2019). Severe damage to the lungs may occur through smoking because the smoker is exposed to significant levels of cadmium. Renal and hepatic damage and coma are also health conditions associated with exposure to high levels of cadmium.

2.2.3 Arsenic (As)

2.2.3.1 Chemistry

Arsenic is one of the fifth group (VA) elements on the periodic table and it is considered a metalloid because it has both metallic and non-metallic properties. It has a relative atomic mass of 74.92 and an atomic number of 33. The oxidation states of arsenic are -3, 0, +3, and +5 but most often it exists in the oxidation state of +3 as arsenite and +5 as arsenate (Pruchnik, 1990). Arsenic affects the environment as well as human health because it exists as an element, inorganic and organic (Jan et al., 2015). Inorganic arsenic is formed when it reacts with sulfur, oxygen, and chlorine to form compounds such as sodium arsenite and arsenic, trichloride arsenic, trioxide arsenic pentoxide, etc. Organic arsenic also reacts with carbon and hydrogen to form compounds including arsenobetaine, dimethylarsinic acid, arsenilic acid, and methylarsonic acid.

2.2.3.2 Sources of Arsenic

Arsenic is present naturally in the environment and also it can be released in large amounts into the environment through volcanic eruptions, forest fires, erosion of rocks, and certain human activities such as smoking, use of cosmetics and drinking of water (Sabine and Wendy, 2009). People are mostly exposed to arsenic by using common products such as pesticides, dyes, paints, drugs, wood preservatives, and soaps. Semi-conductors, fertilizers, and animal feeding operations tend to discharge arsenic into the environment at higher levels (Jaishankar et al., 2014).

2.2.3.3 Toxicity to humans

The toxicity of arsenic is a great concern to toxicologists and health personnel because it causes numerous human health implications. Health conditions caused by exposure to arsenic include skin damage, cancer, and circulatory system problems. Drinking water that contains arsenic above the acceptable limits causes severe clinicopathological diseases, developmental abnormalities, neurobehavioral sickness, and cardiovascular diseases (Mishra et al., 2019). Inorganic arsenic (arsenite and arsenate) are carcinogenic and therefore are a threat to human health since their exposure can lead to cancer of the lungs, liver, bladder, and skin (Jaishankar et al., 2014). In Taiwan, it has been reported that prolonged exposure to inorganic arsenic to people via drinking water has resulted in black foot diseases, where there is severe damage to blood vessels in the lower limbs (Mahurpawar, 2015). Other health conditions such as vomiting, diarrhea, nausea, and darkening of the skin are associated with acute arsenic poisoning.

2.2.4 Mercury (Hg)

2.2.4.1 Chemistry

Mercury is a silvery d-block element that belongs to group 12 and period 6 on the periodic table. It has a relative atomic mass and an atomic number of 200 and 80 respectively. Mercury is the only element that is metal and exists as a liquid at standard temperature and pressure. It has three oxidation states, thus -2, +1, and +2. Mercury exists in mercuric (Hg^{2+}), mercurous (Hg_2^{2+}), elemental (Hg0), or alkylated forms in nature (Mahurpawar, 2015). In addition, mercury mainly is found in metallic elements, inorganic salts, and organic compounds. Mercury has a total of 11 isotopes but seven of the isotopes are stable.

2.2.4.2 Sources of mercury

Anthropogenic activities such as mining, agriculture, municipal wastewater discharge, incineration, and discharge of industrial wastewater are the major source of mercury in the environment (Jaishankar et al., 2014). Other sources of mercury include seafood, fish, and skin whitening cosmetics. Organic mercury specifically methyl mercury(MeHg) enters the body of humans through food especially fish whiles ethyl mercury finds its way into the body as part of vaccine preservatives and some antiseptics (Jan et al., 2015).

2.2.4.3 Toxicity to humans

Toxicity of mercury is greatly based on the form mercury exists, thus elemental mercury, inorganic mercury, or organic mercury. Health conditions such as tremors, emotional disability, memory loss, neuromuscular changes, and headaches are linked to inhalation of elemental mercury vapor (Mahurpawar, 2015). Symptoms associated with exposure to elevated metallic mercury include lung damage, vomiting, nausea, skin rashes, hypertension, and renal dysfunction (Jan et al., 2015). Mercury exposure can also lead to anxiety, fatigue, autoimmune diseases, hair loss, and irritability. Exposure to methyl mercury via the eating of seafood and fish can cause mitochondrial damage, lipid peroxidation, accumulation of neurotoxic molecules, and microtubule destruction (Mishra et al., 2019). Permanent damage to the brain, kidneys, and developing fetuses can occur as a result of elevated levels of mercury (Jan et al., 2015).

2.2.5 Iron (Fe)

2.2.5.1 Chemistry

Iron is a lustrous metal with a grayish tinge, which belongs to group 8 and period 4 on the periodic table. It has a relative atomic mass of 55.8 and an atomic number of 26. It exists mainly in oxidation states of +2 (ferrous) and +3 (ferric). Iron has four stable isotopes and these are ^{54}Fe, ^{56}Fe, ^{57}Fe, and ^{58}Fe (Pruchnik, 1990). It is considered the most reactive element in its group (Pruchnik, 1990).

2.2.5.2 Source of iron

Iron and iron-containing compounds are widely common in the human environment. Iron is usually used in the plastic and textiles industries. It is also in high demand in the cosmetic industry because of its color range (Azeez et al., 2013).

2.2.5.3 Toxicity of iron

Iron is known to be an essential element that plays a vital role in cellular reactions within the body of humans. Although iron is needed by the body to function well, when it exceeds a particular threshold it becomes toxic. The accumulative effect of elevated concentrations of iron in the body leads to cellular destruction and mutation (Borowska and Brzóska, 2015). When iron salts such as iron sulphate, iron sulphate monohydrate, and iron sulphate heptahydrate are exposed to the body through oral, dermal and inhalation means, they are of low severe toxicity (Jaishankar et al., 2014). Ingestion of elevated levels of iron can lead to the production of free iron which causes lipid peroxidation which also results in severe damage to mitochondria, microsomes, and other cellular organelles (Jaishankar et al., 2014).

2.2.6 Nickel (Ni)

2.2.6.1 Chemistry

Nickel is a hard silver metal that belongs to group 10 and period 4 on the period table. It has a relative atomic mass and an atomic number of 58.7 and 28 respectively. The most common oxidation state of nickel is +2 but it can also exist in oxidation states such as 0, +1, and +3 (Pruchnik, 1990).

2.2.6.2 Source of Nickel

Nickel exists in the environment through anthropogenic activities such as metal plating, combustion of fossil fuels, and mining. Humans are exposed to nickel by using products such as cosmetics, detergents, and jewelry. When people eat chocolate and vegetables from polluted soils, they are exposed to high sources of nickel. The Source of nickel also includes breathing contaminated air, drinking water, eating food, and smoking cigarette (Mahurpawra, 2015).

2.2.6.3 Toxicity to humans

When the skin is exposed to nickel it leads to the development of dermatitis also known as "nickel itch" (Mahurpawra, 2015). Hypersensitivity, skin irritation, and nephrotoxicity are conditions related to nickel exposure (Borowska and Brzóska, 2015). A woman from Belgium who used an eye pencil containing nickel experienced itching, dermatitis, erythema, and moderate scaling of both eyelids and infiltration (Borowska and Brzóska, 2015). Humans have a higher tendency of developing lung cancer, nose cancer, larynx cancer, and prostate cancer when exposed to higher levels of nickel (Mahurpawra, 2015).

2.2.7 Chromium (Cr)

2.2.7.1 Chemistry

Chromium is a steely-grey lustrous metal that is found in group 6 and period 4 on the periodic table. It has a relative atomic mass of 52 and an atomic number of 24. The commonest oxidation states of chromium are +3 and +6 followed by +2 (Pruchnik, 1990).

2.2.7.2 Source of chromium

Workers in industries such as metallurgy, electroplating, paint and pigment, tanning, wood preservation, and paper are exposed to chromium since it is the commonest raw material (Jaishankar et al., 2014). Chromium is abundant in rocks, water, air, soil, and food products. Various literature surveys have reported that humans can be exposed to chromium through pharmaceutical drugs and cosmetics.

2.2.7.3 Toxicity to humans

Chromium (VI) compounds are known toxins and are believed to cause cancer in humans. Chromium (III) on the other hand, is an essential nutrient needed by the body to function properly (Sabine and Wendy, 2009). Prolonged use of cosmetics containing chromium (IV) can lead to damage to the kidney, liver, circulatory, and nerve tissues (Sabine and Wendy, 2009). Furthermore, exposure to chromium (VI) can result in conditions such as nasal irritation, rhinitis, pulmonary congestion, and perforated eardrums (Mishra et al., 2019). Excessive exposure to chromium by humans may result in cardiovascular problems, gastrointestinal problems, and hematological conditions as well as renal dysfunction (Sankhla, 2019). When humans drink water containing high levels of chromium, they are likely to experience skin allergies, lung fibrosis, and cancer of the respiratory tract (Sankhla, 2019).

2.3 Heavy metal present in cosmetics

Cosmetics are purposely applied to the body to beautify the physical appearance of an individual. Recently the presence of heavy metals in cosmetics is a worry for clinicians and researchers throughout the world (Feizi et al., 2019). Several studies have reported that different types of cosmetics contain heavy metal(loid)s such as Pd, Cd, Hg, Ni, As, Fe, and Cr (Alam et al., 2019; Amartey et al., 2011; Ekere et al., 2014; Ullah et al., 2017). Cosmetic products are made up of many groups of chemical substances, but the heavy metal group is known to pose health risks to the consumer (Rahil et al., 2019). Parabens and some heavy metals are used as preservatives during the manufacturing process of cosmetic products because of their antibacterial and antifungal properties (Arshad et al., 2020). Heavy metal contamination of cosmetics may occur during the production process or the use of contaminated raw materials (Akpe et al., 2020). Plants materials used as raw materials for producing cosmetics may contaminate cosmetics with heavy metals as a result of pretreatment of the plants with fertilizer and pesticides (Arshad et al., 2020). Heavy metals are intentionally added to cosmetic products in the form of pigments, UV filters, and antiperspirants (Arshad et al., 2020). Cadmium and iron are used in cosmetics products because of their color ranges (Feizi et al., 2019). Research by Nourmoradi et al. (2013) reported that cosmetics such as lipstick, eye shadow, and body power contain varying levels of toxic metals including lead and cadmium (Nourmoradi et al., 2013). Ackah et al. (2015) conducted a survey on nail polish and lipstick which were purchased from shops in Medina, Accra revealed that both nail polish and lipstick samples contain heavy metals such as lead, cadmium, and chromium(Ackah et al., 2015). Another study by Nkansah et al. (2018) also reported that lipstick samples bought from Kumasi central market contain varying levels of lead and cadmium (Nkansah et al., 2018). An investigation of 32 samples of facial cosmetics reported that 90% of samples have heavy metals in varying amounts when they were analyzed (Ukonaku et al., 2020). Cosmetic products such as lipstick, eyeliner, powder, and hair dye were investigated and found to contain toxic metal(loid)s including lead, cadmium, arsenic, and mercury (Nasirudeen and Amaechi, 2015). In Ethiopia, the most common brands of cosmetics such as face powder, cream, lotion, and lipstick were analyzed and the results revealed that almost all the samples contain heavy metals (Mohammed and Habtie, 2019). Heavy metals are common in cosmetic products as impurities because of their ubiquitous nature (Alam et al., 2019)

2.4 Absorption of metals through the skin

Heavy metals in cosmetics can penetrate the skin due to their physical and chemical properties (Elzbieta et al., 2018). Metals in cosmetics can interact with the skin, since most of them are applied directly to the skin, and this leads to the absorption of these metals into the bloodstream and further accumulation of them in various organs in the body (Meng et al., 2021). Although there are numerous routes heavy metals used to enter the human body, dermal contact is considered the most important route (Alam et al., 2019). A study was conducted in Tanzania, between miners who use mercury for amalgamation and people who are not involved in mining activities, the results revealed that both groups of people have mercury in their blood and urine, but the people who are not engaged in mining their mercury levels were derived from cosmetics such as creams and soap (Somaye et al., 2019). Prolong use of cosmetics with heavy metals can result in percutaneous absorption of these metals under hot humid conditions (Orisakwe and Otaraku, 2013). The amount of cosmetic per unit area on the skin and the total time of exposure of the skin to cosmetic has a direct link with the degree of penetration, and therefore the higher the amount of cosmetic and the time of cosmetic on the skin, the higher the rate of absorption (Ukonaku et al., 2020). Toxic metals such as As, Ni, and Cr are stored in the stratum corneum and may lead to allergic contact dermatitis while Hg, Pd, and Fe penetrate the skin layers to the bloodstream and are transported by the blood vessels into different organs where they accumulated and cause toxic effect (Borowska and Brzóska, 2015). The diagram below shows how the metals are accumulated or adsorbed into the bloodstream.

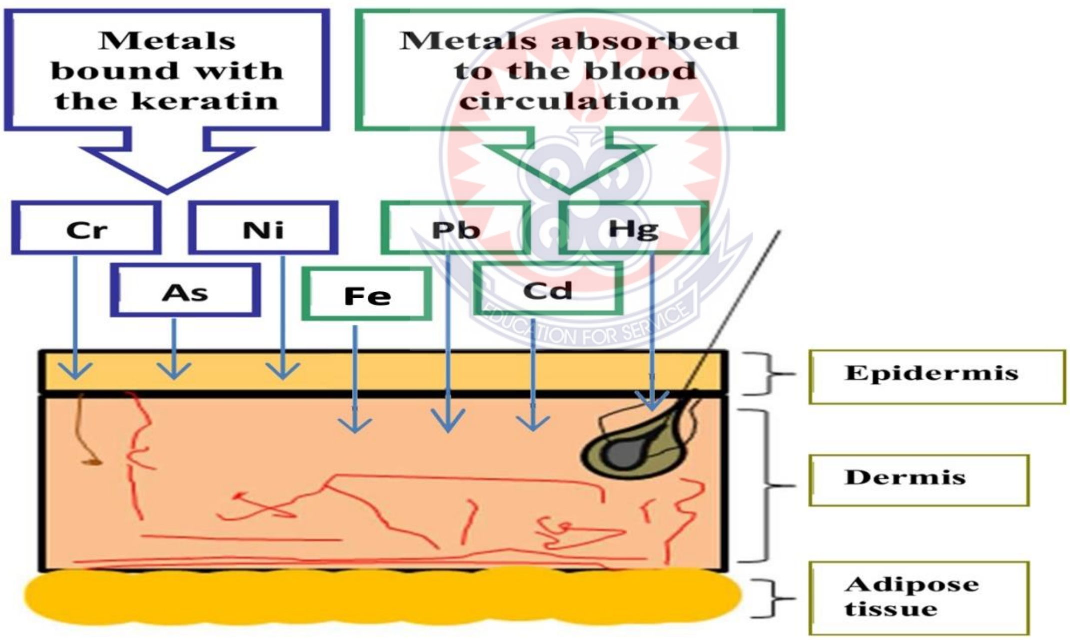

Figure 2.1: Schematic representation of metals accumulation in the skin and their absorption into the bloodstream.

2.5 Heavy metal(loid)s determination

Different analytical techniques are available to determine the metal concentration in cosmetics. Some of the techniques used in the analysis include Atomic Absorption Spectroscopy (AAS), Inductively Coupled Plasma Mass Spectroscopy (ICP-MS), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), Cold Vapor Atomic Fluorescence Spectroscopy (CVAFS), Graphite Flame Atomic Absorption Spectroscopy (GFAAS), Electro-Thermal Atomic Absorption Spectroscopy (ETAAS), Atomic Fluorescence Spectroscopy (AFS), and Hydride Generation Atomic Absorption Spectroscopy (HGAAS). These methods can analyze cosmetic samples by first conducting sample pretreatment which involves the necessary procedures directed to eliminate interferences and concentrate the analyte according to the selected analytical technique to be applied. In selecting an analytical technique for analysis, there are certain factors to consider, some of them include, detection limits, cost, interference, data quality, sample throughput, sensitivity, and availability of the instrument (Ewing, 2005).

2.5.1 Atomic Absorption Spectroscopy (AAS)

This technique is the oldest and the most common in most laboratories used for analyses. In this method, the cosmetic sample can be analyzed by performing sample preparation which involves adding a mixture of concentrated acids such as nitric acid and hydrogen fluoride or sulphuric acid and nitric acid to the sample to convert it to liquid form. Chloric acid or hydrogen peroxide is added for complete oxidative digestion. The sample solution is then aspirated into flames and the element of interest is converted to atomic vapor. The flame contains atoms of the element, and it causes some of the atoms to move to the excited state but most of them remain in the ground state. These atoms in the ground state absorb radiations emitted by the source of the element of interest so its characteristic line is emitted. The amount of radiation absorbed is directly proportional to the wavelength of the flame and the concentration of the atomic vapor. When the wavelength is held constant, the concentration of atomic vapour is equal to the concentration of the element of interest in the sample solution (Nollet and Gelder, 2014). The strengths of this method include, that it is cheap, widely accepted, and easy to use. Moreover, the technique is characterized by a low detection limit and high precision.

2.6 Theory of risk assessment

Humans are regularly exposed to harmful agents via food, water, air, and dermal contact. It is therefore important for a developing country like Ghana to establish a framework to assess and manage risks posed by these harmful agents. Risk assessment is a scientific process that depends on the amount of a chemical present, the exposure of the chemical, and its toxicity in humans or the environment (USEPA, 2000). The risk assessment process begins by collecting measurements that characterize the nature and extent of chemical contamination in the environment, as well as information needed to predict how the contaminants behave in the future (USEPA, 2006). There are four steps in the risk assessment process as seen in the figure below

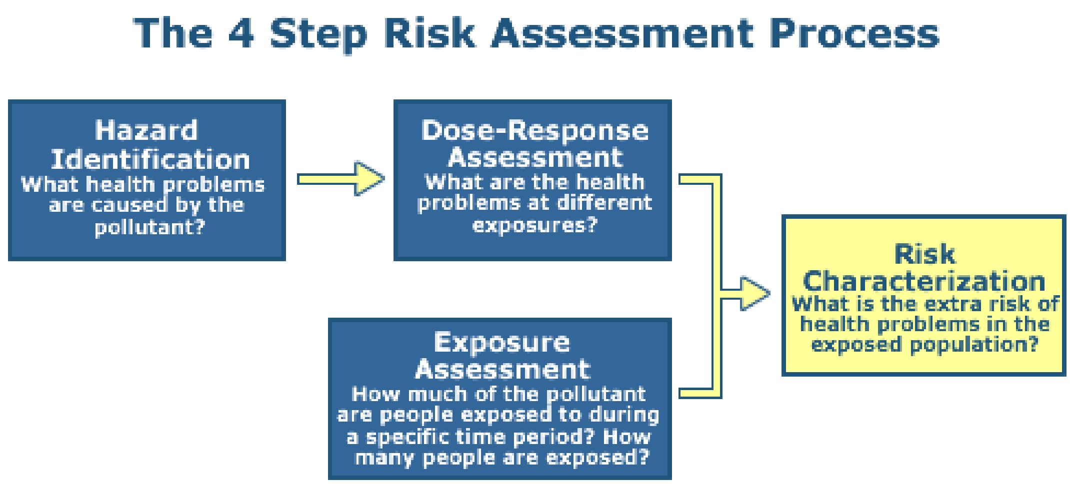

Figure 2.2: Steps of the risk assessment process

2.6.1 Step 1: Hazard Identification

Hazard Identification is the process of determining whether exposure to a harmful agent can cause an increase in the incidence of specific adverse health effects such as cancer, birth defects, etc (USEPA, 2000). In the case of heavy metals, the process examines the available scientific data for a given heavy metal and develops a weight of evidence to characterize the link between the negative effects and the heavy metal (USEPA, 2000). Exposure to heavy metals may generate many different adverse effects in humans including diseases, formation of tumors, reproductive defects, death, and other effects (USEPA, 2006). Mode of action is a sequence of key events and processes, starting with the interaction of an agent and a cell, proceeding through operational and anatomical changes, and resulting in a health condition (USEPA, 2006). The mode of action of heavy metal is based on physical, chemical, and biological information about the metal that helps to explain key events in the metal's influence on the health effects.

2.6.2 Step 2: Dose-response assessment

A dose-response relationship describes how the likelihood and severity of adverse health effects (the responses) are related to the amount and condition of exposure to a heavy metal (the dose provided) (USEPA, 2006). The concentration of the heavy metals in cosmetics samples will be paramount and therefore "concentration-response" relationship will be of significance to the study. Exposure to heavy metals even at low levels in cosmetics still poses a health risk to the consumer because the metals can accumulate in the keratin of the skin (Orisakwe and Otaraku, 2013).

2.6.3 Step 3: Exposure assessment

Exposure assessment is the process of measuring or estimating the magnitude, frequency, and duration of human exposure to heavy metals in the environment (USEPA, 2006). According to the USEPA, exposure is contact between a metal and the visible exterior of a person (e.g. skin and openings into the body). Exposure to a toxic metal can be measured by estimating its concentrations in the environment, considering the models of its chemical transport and fate in the environment, and estimating human intake of the metal over a certain period (USEPA, 2006). Exposure assessment considers both the exposure pathway as well as the exposure route.

2.6.4 Step 4: Risk characterization

Risk characterization conveys the risk assessor's judgment as to the nature and presence or absence of risks, along with information about how the risk was assessed (USEPA, 2000). Risk characterization can simply be defined as the qualitative and/or quantitative evaluation of the nature of the adverse health effects associated with biological, chemical, and physical agents which may be present in food, water, air, or cosmetics. Comprehensive risk characterization involves a multi-dimensional approach where the individual steps conduct their risk characterization plus an integrated analysis of the risk (USEPA, 2006).

2.6.5 Margin of Safety (MoS)

Health risks to humans as a result of exposure to heavy metals present in cosmetic products can be calculated as a Margin of Safety (MoS). MoS is the ratio of the No Observable Adverse Effect Level (NOAEL) to the Systemic Exposure Dosage (SED) as reported previously by (Marinovich et al., 2014). Based on World Health Organization guidelines for drinking water quality, the lowest amount of MoS is 100, and therefore if the MoS content is 100 or greater, it is considered safe (WHO, 2010).

$$\text{MoS} = \text{NOAEL}/\text{SED} \qquad (1)$$

The SED predicts the number of metals that enter the body via different pathways. The formula for calculating SED is given by the expression (Liu et al., 2013):

$$\text{SED (mg/kg/d)} = \frac{Cs \times AA \times SSA \times F \times RF \times BF}{BW} \times 10^{-3} \qquad (2)$$

Where Cs is the concentration of metal in the cosmetic sample (mg/kg), AA is the quantity of cosmetic product applied (g/cm^2), SSA is the Surface area of skin onto which the product is applied (cm^2), F shows the application frequency of a product/day, RF is the retention factor, BF is bio accessibility factor, 10^{-3}, (mg/kg) is used as unit convertor, BW is the average body weight (70 kg) (Ghaderpoori et al., 2020). A level of exposure where no adverse effect is observed is called NOAEL and its value was calculated based on dermal reference dose (RfDs) as reported by (USEPA, 2016) using the expression:

$$NOAEL = RfD \times UF \times MF \quad (3)$$

Where UF is an uncertain factor, MF is modifying factor and defaults values for MF and UF are 1 and 100 respectively.

2.6.6 Non- carcinogenic Risk

The hazard quotient, HQ (non-carcinogenic risk) of the different metals measured in the cosmetics can be computed. The HQ is the ratio of systemic exposure dose (SED) to the chronic reference dose (RfD) of the toxicant (mg/kg/d) as used by (Liu et al., 2013).

$$\text{Non- carcinogenic risk, } HQ = SED_{Dermal} / RfD_{Dermal} \quad (4)$$

If HQ < 1, the exposed population is safe but if HQ > 1, it is unsafe for humans.

The Hazard Index (HI) was computed to determine the total potential non-carcinogenic health effects caused by exposure to different metals in cosmetics (Ghaderpoori et al., 2020). HI is the summation of HQ for all heavy metals under study. If HI < 1, the exposed consumers are safe, if HI > 1, it is considered not safe for human health (Liu et al., 2013).

$$HI = \sum HQ \quad (5)$$

2.6.7 Carcinogenic Risk

The carcinogenic risk (CR) is normally determined for carcinogenic metals. CR is computed using the expression (Meng et al., 2021).

$$CR = SED \times SF \quad (6)$$

Where SF represents the cancer slope factor (mg/kg/d).

2.7 Regulatory bodies

In most countries, a regulatory body is in charge of ensuring that the content of heavy metals in cosmetics manufactured or imported into the country is within the acceptable threshold. In Ghana, for instance, Ghana Food and Drugs Authority (FDA) and Ghana Standard Authority (GSA) are responsible to ensure that cosmetic products on the Ghanaian market are safe. However, the regulations for the various heavy metals vary from one regulatory body to the other. Some of the international regulatory bodies include WHO, USFDA, and the EU. The table below shows the acceptable limits of the various heavy metals by the different regulatory bodies.

Table 2.1: Permissible limits of heavy metals in cosmetics by the different regulatory bodies.

	Heavy Metal(loid)s (ppm)							
	Pd	**Cd**	**Hg**	**As**	**Cr**	**Ni**	**Fe**	**References**
EU	0.5	0.5	-	-	1.0	-	-	Alam et al., 2019
WHO	10	0.3	1.0	-	-	-	-	Alam et al., 2019
USFDA	20.0	-	1.0	3.0	-	-	-	Borowska and Brzóska, 2015

2.8 Volatile Organic Compounds (VOCs)

VOCs are organic compounds that are prone to be volatile at room temperature and they include alkanes, alkenes, aromatics, alcohols, aldehydes, ketones, etc. (Nurmatov et al., 2013). VOCs are pollutants produced by evaporation at room temperature from household products such as paints, cosmetics, pharmaceuticals, cleaning agents, and pesticides (Nurmatov et al., 2013). The cosmetics industry uses VOCs and other ingredients in the manufacture of products such as shampoos, body lotions, creams, lipsticks, deodorants, and perfumes. Some VOCs are toxic to the human body even at trace levels and others are non-degradable hence can bio accumulate in the soil which affects living organisms and the environment (Nurmatov et al., 2013). Several researchers have reported that there is an accelerated level of VOCs in residential areas coupled with an increase in respiratory symptoms, asthma, atopic disease, and reduced lung function (Nurmatov et al., 2013).

2.9 Gas Chromatography (GC)

The gas chromatography technique is used in most laboratories to analyze volatile organic compounds (VOCs). The cosmetic sample is weighed into a standard measuring flask and filled up with methanol. The mixture is shaken gently and then heated at 60°C for 10 min. The sample solutions will subsequently be analyzed for volatile compounds by GC–MS instrument equipped with a split/splitless injector and an MS column. The carrier gas used can either be helium or nitrogen or argon. The volatile compounds are identified based on a comparison of mass spectra with those of the National Institute of Standards and Technology (NIST) GC-MS Libraries. Also, a visual comparison of unknown mass spectra with known compounds reported in the literature can be used to determine the VOCs (Azeez et al., 2013).

CHAPTER THREE

3.0 METHODS AND MATERIALS

3.1 Study Area

Kumasi is Ghana's second largest city and it is the capital of Ashanti region. Kumasi is estimated to be 270 km north of Accra, which is the capital of Ghana and 120 km south east of Sunyani the capital of Bono Region. It is located between latitude 6.35^0 N and 6.40^0 S and longitude 1.30^0 W and 1.35^0 E. The Kumasi Central Market popularly known as Kejetia is in the heart of Kumasi and it is one of the largest open-air markets in West Africa (Ghana Statistical Service, 2014) and it's the centre of trading for Ghana and beyond. The market forms a border to the north with the Kumasi cultural centre and to the North West with the Komfo Anokye teaching hospital. The southern part of the market is also bordered by Adum, the commercial centre of the city. Kejetia generates huge revenue in terms of tax payment to the state due to the presence of diverse businesses operating in the market. It also serves as transport station so there is influx of greater number of people coming from the northern part of Ghana and countries such as Togo, Burkina Faso and Cote D'lvoire patronizing the market. The Kejetia market has over 10,000 stores and stalls. Virtually everything that one wants to purchase can be found in the Kejetia market. The products sold in the market include food stuff, footwear, kente fabrics, cosmetic products, and many more. However, cosmetics sold at Kejetia are either imported from other countries or are locally manufactured.

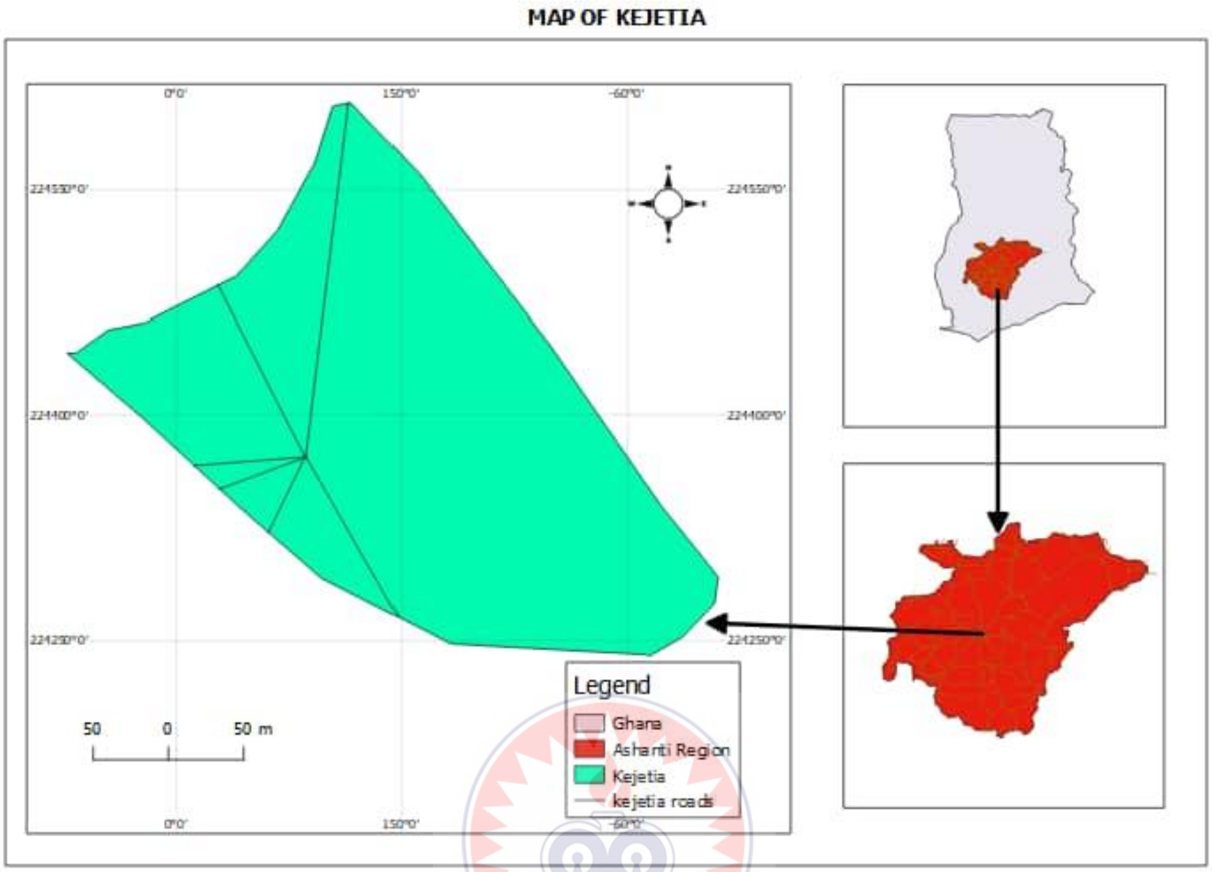

Figure 3.1: A map of Kejetia

3.2 Sampling and collection

A multistage sampling technique was employed. This sampling technique involves the use of two or sampling methods to select a representative sample for analysis. The Kejetia market was divided in five parts and each part represent a cluster. The parts include southern, northern, eastern, western and central. The shops in each cluster were numbered and the researcher selects randomly from the list of numbers which represent shops where the cosmetic products were purchased. The sampling was designed to ensure a maximum number of different brands of cosmetic products are included. In view of their daily use the cosmetics selected include body lotion, cream, eyeliner, and lipstick. Twenty-one including 12 imported and 9 locally manufactured cosmetics were collected (Table 3.1).

Table 3.1: Cosmetics samples and country of origin

Local Cosmetics	Code	Country	Imported Cosmetics	Code	Country
Lotion					
Cocoa care	L1	Ghana	Queen	L4	Cote D'lvoire
Ever sheen	L2	Ghana	Vaseline	L5	USA
Cocoa expert	L3	Ghana	Razac	L6	USA
Cream					
Jra	C1	Ghana	Nivea	C4	Germany
Kakam	C2	Ghana	Blue seal	C5	USA
Habiba	C3	Ghana	Cocoa butter	C6	Cote D'lvoire
Eyeliner					
Huda	E1	Ghana	Curina	E4	China
Malek	E3	Ghana	Kylie	E5	China
			Mac	E6	Canada
Lipstick					
Zaron	LP1	Ghana	Beauty	LP4	Turkey
			Matte	LP5	China
			Mac	LP6	Canada

Plate 3.1: Purchased local cosmetics

Plate 3.2: Purchased imported cosmetics

3.3 Reagents and standards

All reagents used in the experiment were of analytical grade. The reagents used including 65% HNO_3, CH_3OH, EDTA and H_2O_2, were obtained from Spectrascan, Sweden. The standard stock solutions (1000 ppm) of all the metals were purchased from Spectrascan, Sweden. Deionized water was used in preparing all solutions.

3.4 Sample preparation

The wet digestion method was used since all the samples could not conveniently be processed by ash drying. The digestion procedure was employed as described by Amartey et al. (2011) and Ackah et al. (2015). About 0.5 grams of each of the samples were weighed into Teflon beakers. A 7 mL concentrated nitric acid (HNO_3) and 1 mL of hydrogen peroxide (H_2O_2) were added to the samples in a fume chamber. The samples were then loaded on a microwave carousel (Ethos 900, Tokyo, Japan). The vessel cap was secured tightly using an appropriate screw tool. The complete assembly was microwave at a temperature of 200 ^{o}C, pressure of 50 bars, and power of 1000 watts for 21 minutes. Finally, after digestion, the samples were cooled at room temperature and the solution was further diluted by deionized water to the final volume of 50 mL.

Plate 3.3: Microwave digester

3.5 Quality control and assurance

Quality assurance techniques were conducted during the analysis to validate the accuracy and reliability of the results obtained. Standard solutions with concentrations 0.20 mg/kg, 0.50 mg/kg, 1.00 mg/kg 2.00 mg/kg and 3.00 mg/kg were prepared and used to obtained calibrations curves. Periodically the accuracy was checked by analyzing the 1.00 mg/kg standard. An accuracy of ± 10% is considered acceptable. All plastic and glassware were washed with detergents, rinsed many times with tap water, and then soaked in 5% HNO_3 solution for 24 hours and followed by rinsing with deionized water before use. Samples were kept in test tubes with corks to avoid contamination. Reagent blank determinations were used to correct the instrument readings. A recovery study was performed by spiking and homogenizing several analyzed samples with varying amounts of standard solutions of the heavy metals. A blank sample was injected into atomic absorption ten times. The limit of detection (LOD) was calculated as LOD = 3 S and the limit of quantification (LOQ) was calculated as LOQ = 10 S, where S is the standard deviation. Linearity study was performed by calibrating of flame atomic absorption spectrometer was performed by introducing different concentrations such as 0.20 mg/kg, 0.50 mg/kg, 1.00 mg/kg 2.00 mg/kg and 3.00 mg/kg of every element standard solution.

3.6 Heavy metal(loid)s analysis

Atomic absorption spectroscopy (AAS Varian SpectrAA model 240FS, Tokyo, Japan) was used in the analysis of lead, nickel, cadmium, chromium, arsenic, mercury and iron. However, the cold vapor technique coupled to AAS was used to estimate mercury. Prior to analysis, standard metal solutions were prepared in five different concentrations 0.20 mg/kg, 0.50 mg/kg, 1.00 mg/kg 2.00 mg/kg and 3.00 mg/kg by serial dilution to obtain a calibration curve for quantitative analysis. 1 ml of each cosmetic sample solution was kept in the sample holder in the instrument and the atomization temperatures of each metal were adjusted. The concentrations of the metals in the sample solutions were determined from calibration curves of absorbance versus concentration of the standard solutions. Each sample was analyzed in triplicate and the concentration of the metals present was displayed in milligram per kilogram (mg/kg) by the instrument.

3.7 Health risk assessment of heavy metal(loid)s

The health risk assessment of the heavy metals present in the various cosmetics samples was done by using the mean concentrations of these metals measured to calculate the Margin of Safety (MoS), Non-carcinogenic risk (Hazard Quotient and Hazard Index), and carcinogenic risk (CR). The equations below were used for the computation (Ghaderpoori et al., 2019).

$$MoS = \frac{NOAEL}{SED} \quad \ldots\ldots\ldots\ldots \text{Equation 1}$$

Where NOAEL = No Observable Adverse Effect Level (SCCS, 2012).

SED = Systemic Exposure Dosage

SED (mg/kg/d) = $\frac{Cs \times AA \times SSA \times F \times RF \times BF}{BW} \times 10^{-3}$ ……………………Equation 2

Where Cs is the concentration of metal in the cosmetic sample (mg/kg), AA is the quantity of cosmetic product applied (g/cm^2), SSA is the Surface area of skin onto which the product is applied (cm^2), F shows the application frequency of a product/day, RF is the retention factor, BF is bio accessibility factor, 10^{-3}, (mg/kg) is used as unit convertor, BW is the average body weight (70 kg).

NOAEL = RfD × UF × MF ……………………………………………Equation 3

Where UF is an uncertainty factor, MF is modifying factor, and defaults values for MF and UF are 1 and 100 respectively.

Hazard Quotient (HQ) = $\frac{SED}{RfD}$ ……………………………………………Equation 4

Where RfD = Reference Dose

Hazard Index (HI) = ∑ HQ ………………………………………….. Equation 5

Carcinogenic Risk (CR) = SED × SF ………………………………….. Equation 6

Where SF = cancer slope factor (mg/kg/d).

3.8 Determination of Volatile Organic Compounds (VOCs)

About 1 g of each cosmetic sample was taken into a test tube and 5 ml of methanol is added. The mixture was heated in a water bath at 37 ^{0}C for 10 minutes. 0.5 ml of 0.1 M EDTA was added to the mixture and then vortexed. The mixture was then sonicated for 30 minutes and further centrifuged at 1370 rpm for 10 minutes. The sample solutions were subsequently analyzed for volatile compounds by GC–MS (GC, Varian 3400CX, Japan) instrument equipped with a split/splitless injector and a Rtix 5 MS column. The carrier gas was helium using the line-of-sight interface kept at 260 °C and the ion-source temperature was set to 250 °C. The volatile compounds were identified based on a comparison of mass spectra with those of the National Institute of Standards and Technology (NIST) v 2.2 (2014) GC-MS Libraries. In addition, a visual comparison of unknown mass spectra with known compounds was reported in the literature and comparisons of the mass spectra of commercially available standards with the unknowns.

Plate 3.4: Samples been sonicated

3.9 Statistical analysis

The data were analyzed using the Statistical Package for the Social Science (SPSS) ver 20. Descriptive statistical parameters such as mean and standard deviation (SD) were used to describe the heavy metal concentration in the cosmetic samples. Microsoft excel was also used to analyze the data in graphs. Kruskal Wallis test was used to determine if there is a significant difference between the mean concentrations of heavy metals in locally manufactured and imported cosmetics at a significance level of $p < 0.05$. Experiments were carried out in triplicate.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Recovery studies

The results of recovery study were within the acceptable range verifying the validity of the proposed method for analysis. The recoveries for the metal(loid)s as well as their LOD and LOQ were shown in Table 4.1.

Table 4.1: Results of recovery studies and LOD and LOQ

Metals	Un-spiked amount (mg/kg)	Amount added (mgkg)	Spiked amount (mg/kg)	Recovery %	LOD (mg/kg)	LOQ (mg/kg)
Pb	2.7±0.02	8.0	10.5	98.85	0.16	0.539
Cd	1.5±0.00	5.0	6.4	99.45	0.06	0.539
As	0.4±0.01	4.0	4.3	96.68	0.029	0.097
Fe	0.3±0.01	2.0	2.2	97.36	0.016	0.054
Ni	0.2±0.00	1.0	1.1	92.49	0.001	0.050
Cr	0.2±0.01	3.0	5.0	95.50	0.015	0.050
Hg	0.5±0.02	2.0	2.3	94.69	0.07	0.054

4.2 Concentration of heavy metal(loid)s in cosmetics

The study analyzed seven (7) metals in 21 cosmetics products. The metal(loid)s included Pb, Cd, As, Fe, Ni, Cr, and Hg. The cosmetic products comprise nine (9) local products and twelve (12) imported products.

4.2.1 Heavy metal(loid)s in lotion

A total of 6 different brands of lotion samples were analyzed. For the case of the local samples, the sample with the highest concentration (11.09±6.30 mg/kg) was found in L3 for As whiles the lowest concentration (0.06±2.14 mg/kg) was found in L2 for Pb. The order of decrease for the imported samples for As is L3 > L2 > L1 for the concentrations 11.09±6.30, 10.02±3.30, 9.56±4.21 mg/kg respectively. However, Ni was the only metal whose concentration was not detected in all the local samples (Table 4.2). It is worth noting that the concentration of Hg in all local samples of lotion (6.55±2.10 mg/kg) was higher as compared to the other metals. An imported lotion sample L5 has the maximum concentration (12.95±7.85 mg/kg) for Pb whiles the minimum concentration BDL is found in L4 for Ni. The order of decrease for the imported samples for Pb was L5 > L4 > L6 for the concentrations 12.95±7.85, 10.23±5.23, and 2.95±0.98 mg/kg respectively.

Table 4.2: Concentration (mg/kg) of heavy metal(loid)s in lotion samples

Sample ID	Pb	Cd	As	Fe	Ni	Cr	Hg
L1	0.23±0.70	1.25±1.20	9.56±4.21	1.05±0.98	BDL	0.09±1.20	6.55±2.10
L2	0.06±2.14	0.90±2.30	10.02±3.30	2.21±1.56	BDL	0.80±0.10	6.21±1.12
L3	1.01±0.9	0.49±0.91	11.09±6.30	0.85±0.56	BDL	0.36±0.84	5.45±1.25
Mean	0.43±0.51	0.88±0.38	10.05±2.29	1.50±0.58	BDL	0.41±0.35	6.24±1.20
L4	10.23±5.23	6.57±6.12	4.96±3.24	8.85±5.02	BDL	6.65±4.15	0.77±0.85
L5	12.95±7.85	8.75±6.30	6.86±4.56	9.24±6.87	0.01±0.20	11.74±8.25	2.15±1.12
L6	2.95±0.98	1.36±0.56	5.35±3.96	3.25±2.45	0.01±0.00	4.65±2.28	1.99±1.02
Mean	8.71±5.17	5.55±3.80	5.72±0.99	7.11±3.35	0.01±0.00	7.68±3.67	1.63±0.76

4.2.2 Heavy metal(loid)s in creams

The maximum concentration (9.10±3.68 mg/kg) was found in C2 for Hg and the minimum concentration BDL was found in C1 and C2 for Ni (Table 4.3). The increasing order of the concentration of Hg for the local samples was C1< C3 <C2. For the imported cream samples, the maximum concentration and minimum concentration were 9.95±7.56 mg/kg and 0.01±0.01mg/kg respectively, and interestingly they were found in the same sample C6 for Pb and Cr. The increasing order of Pb concentration for the samples was C4 <C5< C6 and 3.47±2.14, 5.15±4.25, 9.95±7.56 mg/kg respectively

Table 4.3: Concentration (mg/kg) of heavy metal(loid)s in cream samples

Sample ID	Pb	Cd	As	Fe	Ni	Cr	Hg
C1	2.37±0.86	3.88±1.25	0.79±0.58	0.01±0.02	BDL	0.56±0.48	7.13±2.10
C2	1.60±1.10	4.75±2.29	1.98±0.98	0.02±0.10	BDL	0.26±0.30	9.10±3.68
C3	0.74±0.48	0.85±0.76	0.96±0.85	0.06±0.34	0.01±0.00	0.16±0.33	9.08±4.01
Mean	1.57±0.81	3.16±2.05	1.25±0.65	0.04±0.00	0.01±0.00	0.33±0.21	8.25±1.96
C4	3.47±2.14	2.85±1.75	1.52±0.98	1.11±1.12	0.02±0.00	6.23±4.95	4.59±3.54
C5	5.15±4.25	2.37±1.98	0.76±0.75	1.12±0.84	0.02±0.00	2.95±1.45	6.85±5.23
C6	9.95±7.56	5.87±4.96	7.86±6.73	5.32±4.20	0.01±0.01	5.98±4.56	3.65±2.85
Mean	6.19±3.37	3.69±1.90	3.38±3.90	2.51±2.43	0.02±0.01	5.05±1.83	5.03±1.64

4.2.3 Heavy metal(loid)s in eyeliners

The eyeliner samples were 5 in number. The local products had a maximum concentration (9.35±0.21 mg/kg) found in E3 for As whiles the minimum concentration (0.00±0.00 mg/kg) was found in E1 and E3 for Ni (Table 4.4). The imported samples have a maximum concentration (15.85±10.23 mg/kg) found in E4 for Pb. Surprisingly, all three samples of eyeliner were BDL. The decreasing order of the concentration of Pb for the imported samples was E4 > E5 > E6.

Table 4.4: Concentration (mg/kg) of heavy metal(loid)s in eyeliner samples

Sample ID	Pb	Cd	As	Fe	Ni	Cr	Hg
E1	0.49±0.37	3.26±2.02	9.07±0.02	6.52±2.03	BDL	1.13±1.00	0.36±025
E3	1.95±1.36	0.76±0.54	9.35±0.21	6.78±3.02	BDL	1.65±0.96	0.17±0.15
Mean	1.22±1.03	2.00±1.77	9.23±0.19	9.23±0.19	BDL	1.39±0.37	0.26±0.13
E4	15.85±10.23	5.96±4.56	6.25±3.68	6.84±4.58	BDL	4.63±2.45	2.15±1.87
E5	10.55±1.24	1.89±0.87	3.73±1.02	4.03±0.98	BDL	5.93±3.36	1.46±0.78
E6	8.760±6.26	5.83±4.85	6.79±5.14	7.33±5.59	BDL	4.25±2.95	1.93±0.85
Mean	9.05±4.65	4.56±2.31	4.92±2.78	5.07±3.50	BDL	4.94±0.88	1.84±0.35

4.2.4 Heavy metal(loid)s in lipsticks

Four lipstick samples were assessed. The local lipstick sample was only one and among the metals, Fe has the highest concentration (9.87±5.23 mg/kg) and the lowest concentration (0.01±0.00 mg/kg) was seen in Ni. The concentration of the metals in the only lipstick sample decreases in the order Fe > Cr > Pb > As > Cd (Table 4.5). However, Hg was not detected in the sample. For the imported lipstick, the maximum concentration and minimum concentrations are 16.95±6.57 mg/kg and BDL for Fe and Ni respectively. The maximum concentration was found in LP6 whereas the minimum concentration was found in LP4. The increasing order of the concentration of Fe for the imported samples was LP4< LP5 < LP6.

Table 4.5: Concentration (mg/kg) of heavy metal(loid)s in lipstick samples

Sample ID	Pb	Cd	As	Fe	Ni	Cr	Hg
LP1	5.69±3.85	2.49±1.56	3.62±1.98	9.87±5.23	0.01±0.00	7.26±4.96	BDL
Mean	5.69±3.85	2.49±1.56	3.62±1.98	9.87±5.23	0.01±0.00	7.26±4.96	BDL
LP4	17.64±11.23	10.75±7.56	9.26±7.84	10.76±9.63	BDL	6.24±4.68	BDL
LP5	13.68±10.54	11.01±9.52	8.56±6.60	14.65±7.12	0.010±0.01	6.60±5.65	BDL
LP6	14.78±8.61	8.97±6.78	7.51±5.15	16.95±6.57	0.010±0.00	5.86±1.95	BDL
Mean	13.03±2.00	9.58±1.25	8.11±0.99	12.98±6.12	0.10±0.00	5.56±1.49	BDL

4.3 Mean concentration of heavy metal(loid)s in cosmetics

The mean concentrations of seven (7) metals investigated in cosmetic products are depicted in the Table 4.6.

Table 4.6: Mean concentration (mg/kg) of heavy metal(loid)s in cosmetics

Cosmetic	Pb	Cd	As	Fe	Ni	Cr	Hg
Local							
Lotion	0.43±0.51	0.88±0.38	10.05±0.29	1.50±0.58	BDL	0.41±0.35	6.24±0.20
Cream	1.57±0.81	3.16±2.05	1.25±0.65	0.04±0.00	BDL	0.33±0.21	8.25±1.96
Eyeliner	1.22±1.03	2.00±1.77	9.23±0.19	6.85±2.54	BDL	1.39±0.37	0.26±0.13
Lipstick	5.69±3.85	2.49±1.56	3.62±1.98	9.87±5.23	0.01±0.00	7.26±4.96	BDL
Imported							
Lotion	8.71±5.17	5.55±3.80	5.72±0.99	7.11±3.35	0.01±0.00	7.68±3.67	1.63±0.76
Cream	6.19±3.37	3.69±1.90	3.38±3.90	2.51±2.43	0.02±0.01	5.05±1.83	5.03±1.64
Eyeliner	9.05±4.65	4.56±2.31	4.92±2.78	5.07±3.50	BDL	4.94±0.88	1.84±0.35
Lipstick	13.03±2.00	9.58±1.25	8.11±0.99	12.98±6.12	BDL	5.56±1.49	BDL

4.3.1 Pb concentration

Pb contamination has continued to be a threat to human lives due to high levels of Pb being reported by other studies on different brands of cosmetics (Alam et al., 2019, Ghaderpoori et al., 2019). The range of the mean concentration of Pb for local samples was 0.43±0.51 - 5.69±3.85 mg/kg while the range of the mean concentration of Pb in imported samples was 6.19±3.37 - 13.03±2.00 mg/kg. The results of this study indicated that the maximum mean concentration of Pb was found in the imported lipstick sample. The minimum mean concentration of Pb was recorded in local lotion samples (Figure 4.1). Comparatively, the mean Pb concentration was higher in imported cosmetic samples than in the locally manufactured samples. Order of Pb mean concentration in the local samples was lipstick > cream > eyeliner > lotion whiles the Pb mean concentration in imported samples decreased from lipstick > eyeliner > lotion > cream. Besides, there was no significant difference ($p > 0.05$) between the mean concentrations of local and imported cosmetics. The concentration of Pb obtained in this study is lower than the concentration of Pb reported by Ghaderpoori et al., (2019). On the contrary, Adepoju-Bello et al. (2012) reported far lower values for the concentration of Pb in lipstick and cream samples. The findings are consistent with Ullah et al. (2013), who analyzed Pb in lipstick and body cream.

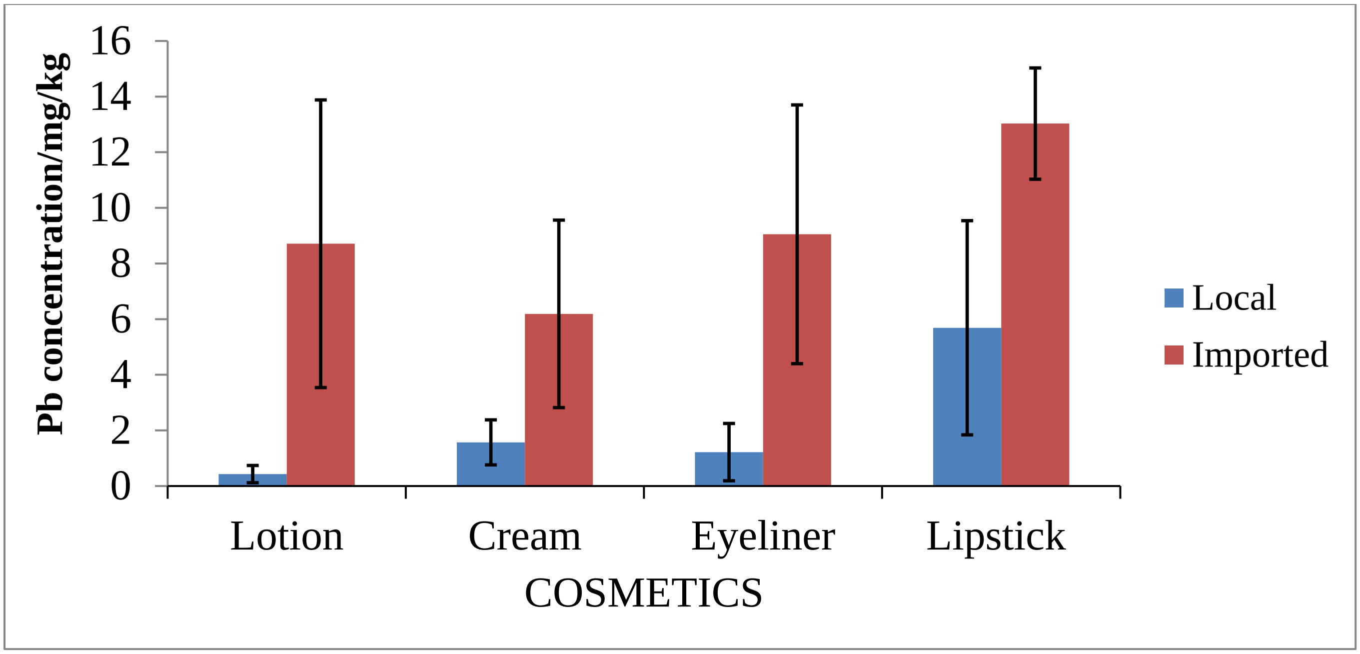

Figure 4.1: Pb concentrations (mg/kg) in cosmetic samples

4.3.2 Cd concentration

Cadmium exposure in cosmetics via dermal contact has been linked to various adverse effects notable among them is cancer. The range of Cd mean concentrations in the local cosmetic samples was 0.88±0.38 - 3.16±2.05 mg/kg whiles the range of Cd mean concentration in imported cosmetic samples was 3.69±1.90 - 9.58±1.25 mg/kg. This study found that the maximum and minimum Cd mean concentrations were found in imported lipstick and local lotion samples respectively (Figure 4.2). Although the mean concentration of Cd was higher in imported cosmetic samples than in local samples, there was no significant difference between the means of local and imported cosmetics. The decreasing order of Cd mean concentrations in local samples was cream > lipstick > eyeliner > lotion. The decreasing order of Cd means concentration in imported samples was also lipstick > lotion > eyeliner > cream. Yoeza and co-workers analyzed Cd levels in cosmetics samples including lipstick, eyeliner, and foundation, and found the range of the level of Cd as ND – 23.78 mg/kg (Yoeza et al., 2018). The findings of

Yoeza and co-workers were seen to be higher than the findings of this study. However, the results of this study are contrary to those of Rajagopal et al. (2015), whose study could not detect Cd in all cosmetics samples. The results of this are in agreement with those obtained by Aminat et al. (Aminat et al., 2019).

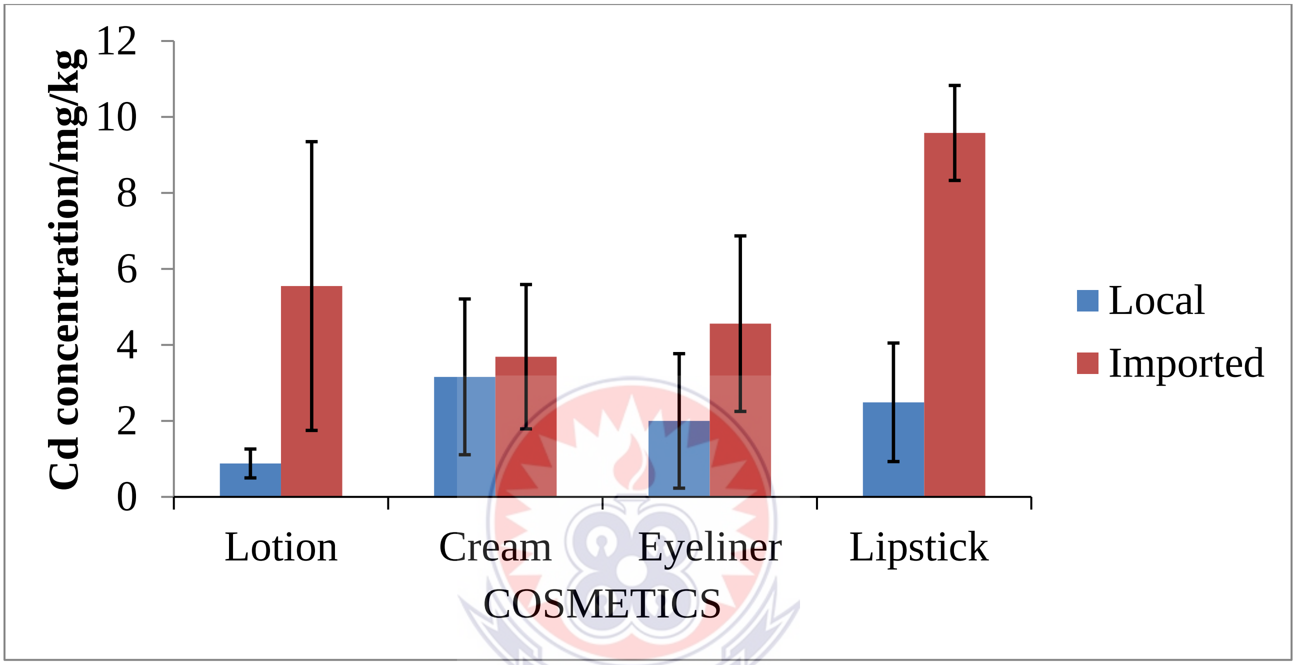

Figure 4.2: Cd concentration (mg/kg) in cosmetic samples

4.3.3 As concentration

People are mostly exposed to arsenic by using common products such as pesticides, herbicides, paints, wood preservatives, and cosmetics. Inorganic arsenic is a source of carcinogen which causes cancer to the skin, lungs, liver, and bladder (Sabine and Wendy, 2009). The maximum and minimum mean As concentrations were 10.05±0.29 mg/kg and 1.25±0.65 mg/kg respectively, which were found in local cosmetics products (lotion and cream) as seen in Figure 4.3. However, from the Kruskal Wallis test, the mean difference between local and imported cosmetics was not statistically significant despite the elevated As mean concentrations of local cosmetics to imported cosmetics. The order of As mean level in local and imported cosmetics products were lotion > eyeliner > lipstick > cream and lipstick > lotion > eyeliner > cream respectively. The mean concentration of this study was lower than those reported by Nasirudeen and Ameachi. (2015) and Adejupo- Bello et al. (2012) (Nasirudeen and Ameachi., 2015, Adejupo-Bello et al., 2012). However, the As level in both cosmetics are similar with those reported by Nancy et al. (Nancy et al., 2014).

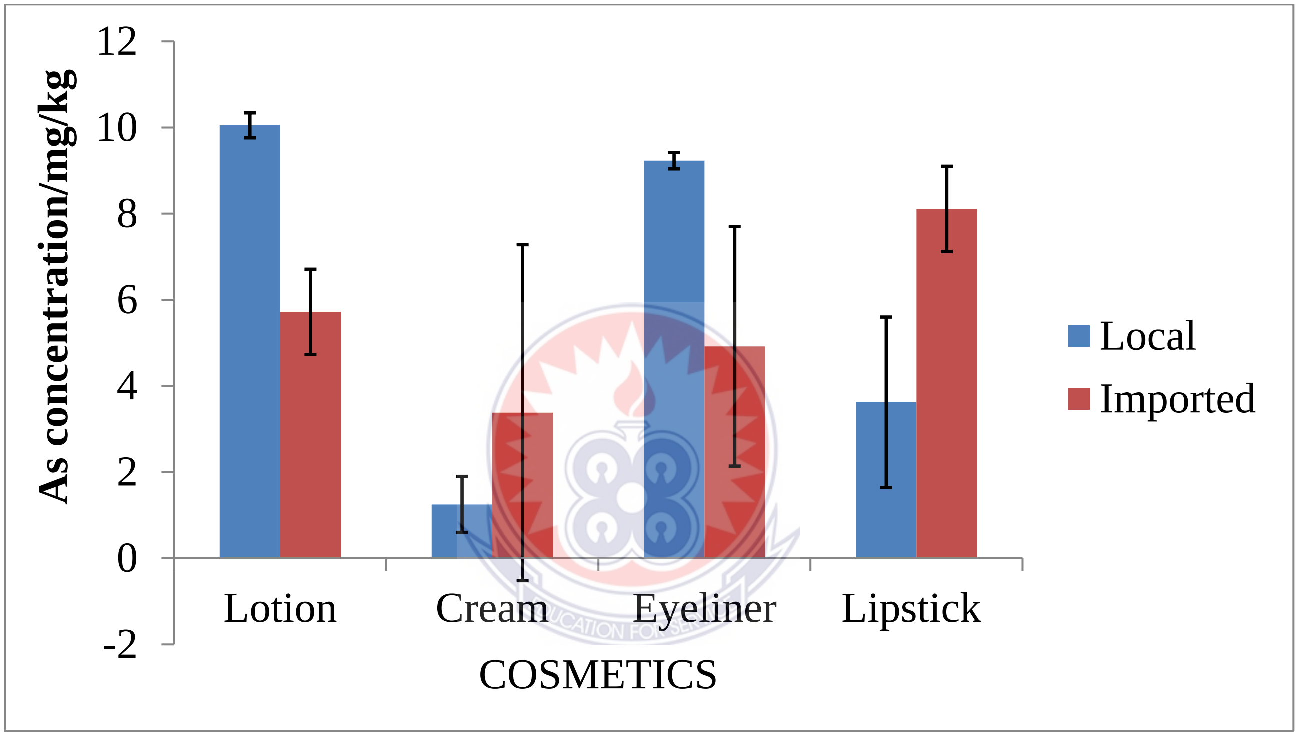

Figure 4.3: As concentration (mg/kg) in cosmetic samples

4.3.4 Fe concentration

There is high demand for Fe in the cosmetic industry because of its color range. Although Fe is needed by the body to function well, when it is above a particular threshold it becomes toxic. According to the results, the Fe level was higher in cosmetics products that come in different colors. For example lipstick and eyeliner. The maximum Fe concentration was found in imported lipstick whiles the minimum Fe level was found in the local cream sample (Figure 4.4). The mean concentrations of Fe in both local and imported cosmetics products were not similar but there was no significant difference between the means. The increasing order of Fe level in local cosmetics was cream < lotion < eyeliner < lipstick, whiles the same order can be seen in imported cosmetics as cream < eyeliner < lotion < lipstick. The accumulative effect of elevated concentrations of Fe in the body leads to cellular destruction and mutation (Magaye et al., 2014). Although the Fe concentration of this study differs from some published studies Ekere et al., 2014, Ebietal et al., 2018, they are consistent with existing data (Ashad et al., 2020).

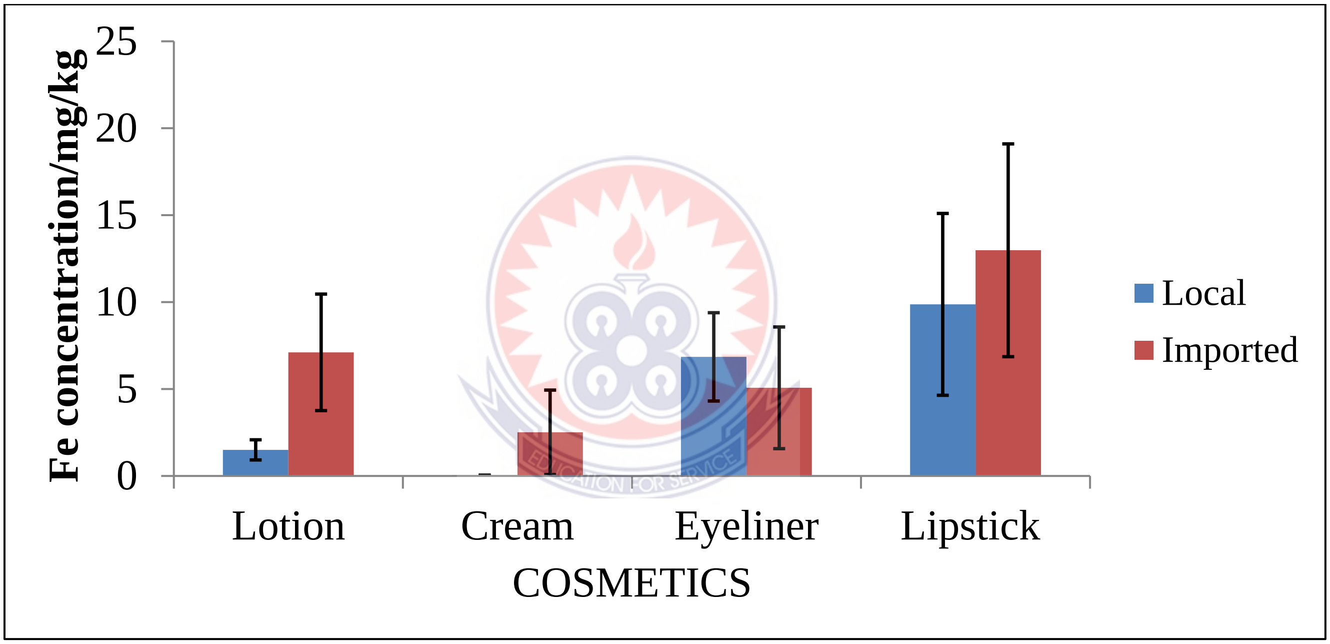

Figure 4.4: Fe concentration (mg/kg) in cosmetics samples

4.3.5 Ni concentration

Humans are exposed to nickel by using products such as cosmetics, detergents, and jewelry. Dermal exposure is one of the most significant routes through which heavy metals in cosmetics enter the body since they are applied directly to the skin (Ullah et al., 2013). It is interesting to note that Ni mean concentrations were very low as compared to the other metals assessed (Figure

4.5). The Ni concentration range for both local and imported was BDL - 0.02±0.01 mg/kg. Even though the Ni concentration in the cosmetic samples was low, the repeated use of cosmetics can lead to bioaccumulation of metals in the body which may result in adverse effects such as hypersensitivity, skin irritation, and nephrotoxicity (Somaye et al., 2019). There was no significant difference between the Ni concentrations in local and imported cosmetics. A woman from Belgium who used an eye pencil containing Ni experienced itching, dermatitis, erythema, and moderate scaling of both eyelids and infiltration (Somaye et al., 2019).

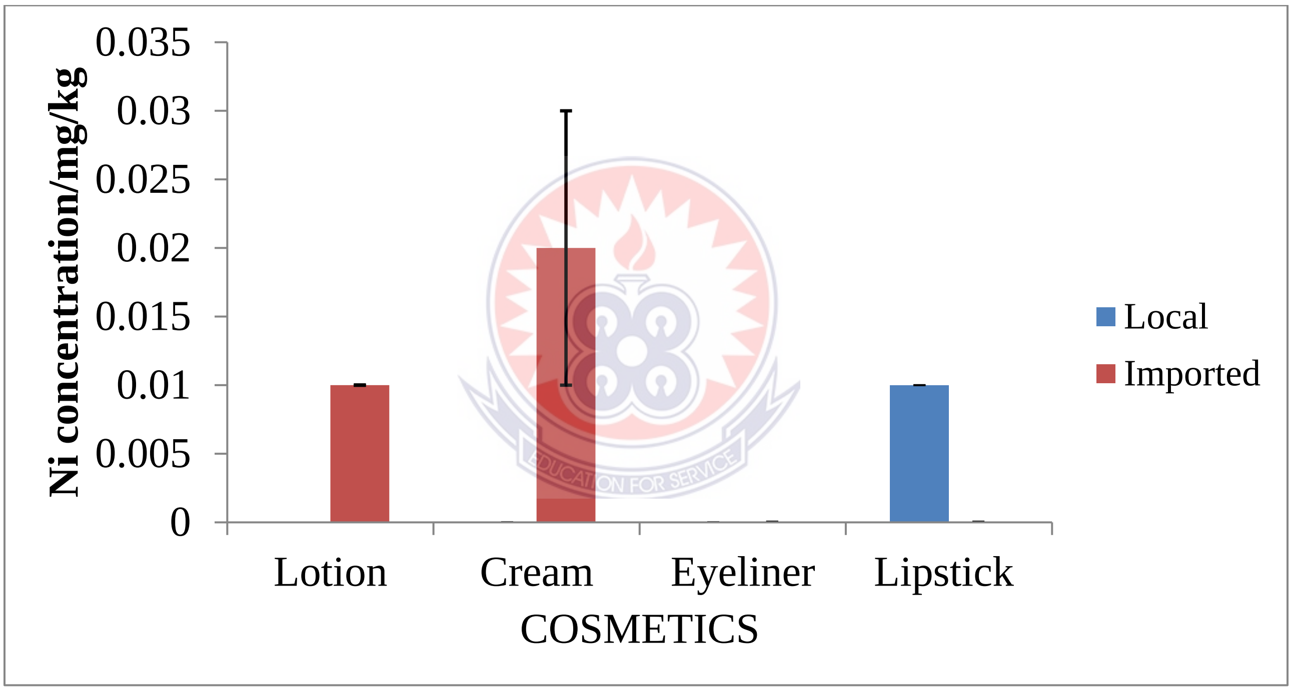

Figure 4.5: Ni concentration (mg/kg) in cosmetic samples

4.3.6 Cr concentration

Chromium (VI) compounds are known toxins and are believed to cause cancer in humans. Chromium (III) on the other hand, is an essential nutrient needed by the body to function properly. Accelerated levels of chromium can cause skin ulcers and other allergic reactions producing redness and swollen skin. Prolonged use of cosmetics containing chromium (IV) can lead to damage to the kidney, liver, circulatory system, and nerve tissues (Sabine and Wendy, 2009). According to the results, the Cr concentration in the imported cosmetic was higher than the locally made cosmetics (figure 4.6). The maximum and minimum Cr concentration in local cosmetic samples was 0.33±0.21mg/kg (cream) and 7.26±4.96 mg/kg (lipstick) respectively. For the imported cosmetics, the maximum concentration was 7.68±3.67 mg/kg (lotion) while the minimum was 4.94±0.88 mg/kg (eyeliner). Additionally, there was no significant difference between the Cr concentration in local and imported cosmetics. The order of Cr concentration in local cosmetics was lipstick > eyeliner > lotion > cream while the order in imported cosmetics was lotion > lipstick > cream > eyeliner. Moreover, the result reflects those of Usman et al. (2021) who determine the Cr concentration in cosmetics such as lipstick, eyeliner, and body cream. The Cr levels observed in this investigation were far below those observed by Nancy and her co-workers (Nancy et al., 2014). Arshad et al. (2020) reported very low Cr concentrations in some imported lotion brands and this result contradicts the finding of this study.

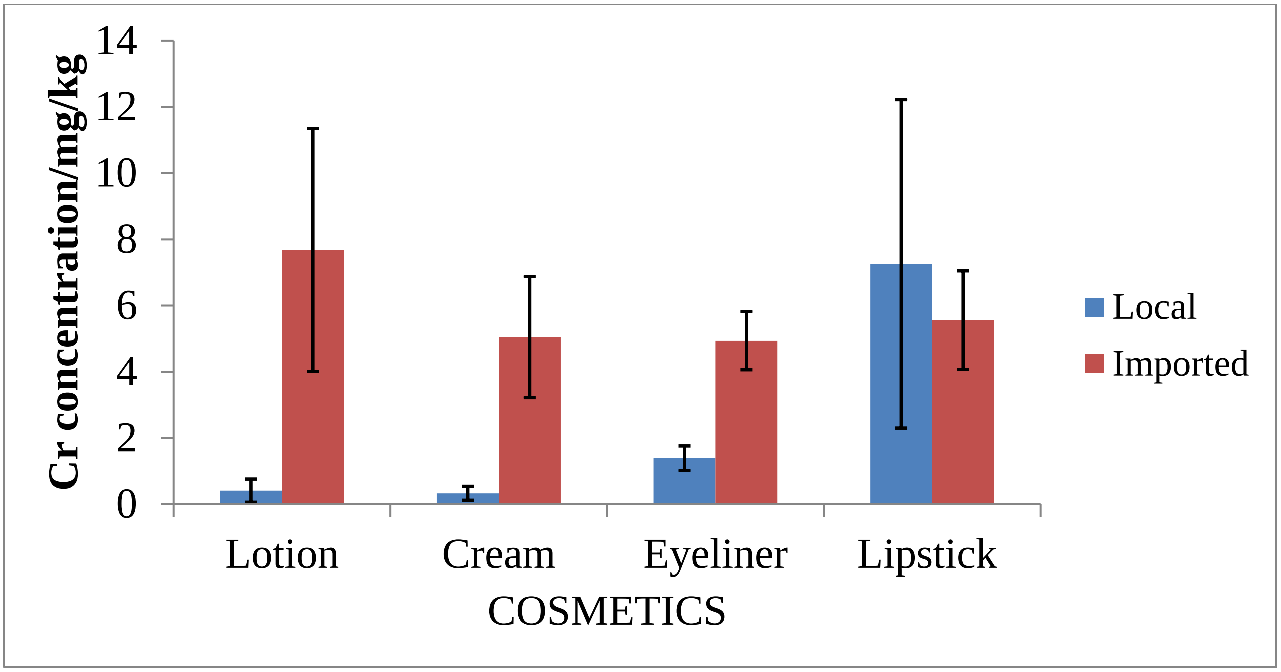

Figure 4.6: Cr concentrations (mg/kg) in cosmetic samples

4.3.7 Hg concentration

Mercury is used in skin-lightening cosmetics such as soap and body creams. Mercury found in cosmetic products is absorbed through the skin and accumulates in the body which results in severe poisoning. However, long-term exposure to very low levels of mercury can lead to chronic neurological and kidney diseases (Agorku et al., 2016). People who use cosmetics containing mercury, even at trace levels experience skin rashes, skin discoloration, and low skin resistance to microbes (Kahairi et al., 2016). Surprisingly, Hg was not detected in both local and imported lipstick. The disparities between the Hg concentration in local and imported cosmetic was not much. The maximum Hg concentrations in local cosmetics as well as in imported were all found in cream. This confirms the higher usage of Hg in body creams. The minimum Hg concentrations were also found in eyeliner and lotion for local and imported cosmetics respectively (Figure 4.7). The order of Hg concentration in local was eyeliner < lotion < cream and the order for imported cosmetics was lotion < eyeliner < cream. The concentrations of Hg were not statistically significant in both local and imported cosmetics. Ghaderpoori and co-workers investigated the level of Hg in cosmetics such as cream, lipstick, and eye pencil. The findings of their work reported the Hg level range as, ND – 0.00077 mg/kg (Ghaderpoori et al., 2020) and these findings are far below the findings of this study. The results of Yoeza et al. (2018) and Nasirudeen et al. (2015) were higher than the results of this study.

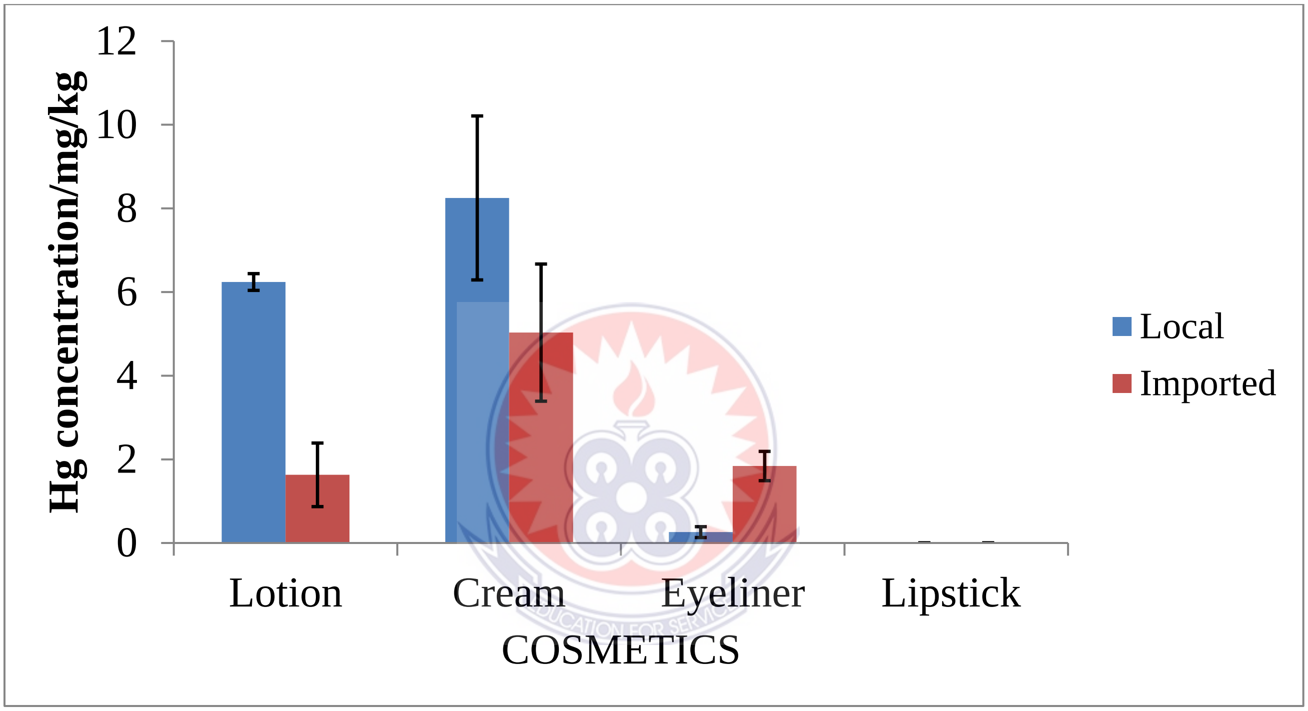

Figure 4.7: Hg concentrations (mg/kg) in cosmetic samples

4.4 International Regulatory bodies

The use of cosmetics as a routine daily body care product dates back to ancient times (Zainy, 2017) but the main issue affecting the cosmetic industry today is the presence of heavy metals. Therefore, international regulatory bodies including WHO, US-FDA, and EU have set various acceptable thresholds for heavy metals in cosmetics. However, the regulations for the various heavy metals vary from one regulatory body to the other. From Figure 4.8, it is observed the concentration of Pb in all the cosmetic samples except local lotion was above the EU threshold of 0.5 mg/kg. According to the WHO, the acceptable limit for Pb in cosmetics is 10 mg/kg. It is worth mentioning that only one cosmetic sample (imported lipstick) had Pb content above the WHO limit. Moreover, the Pb content in all cosmetic samples were below the permissible limit set by US-FDA (Figure 4.8). All samples cosmetics had the Cd content to be more than the acceptable limit of Cd given by the EU (0.5 mg/kg). The levels of Cd were above the WHO limit of 0.3 mg/kg (Figure 4.9). Hg content was detected in six (6) samples; only one cosmetic sample (local eyeliner) had Hg level below 1.0 mg/kg given by WHO (WHO, 2010). However, the rest of the cosmetic samples had Hg content above the permissible limit set by WHO (Figure 4.10). The content of Hg in all cosmetic samples was also more than the US-FDA threshold of 1.0 mg/kg. The Cr level in local lotion and cream was below the EU limit of 1.0 mg/kg and the rest of the other cosmetic samples were above the EU limit for Cr. These results are consistent with Alam et al. (Alam et al., 2019). The average concentration of As in local cream was 1.25±0.65 mg/kg, which is well below the acceptable limit by US-FDA.

Generally, the concentrations of the heavy metals including Pb, Cd, As Cr, and Hg were above some of the international regulatory body’s thresholds. This, therefore, indicates that people who patronize these cosmetic products are at a higher risk. The broad health implications associated with accelerated levels of metals in cosmetics include low IQ, renal cancer, liver cancer, genetic disorder, memory loss, nausea, cellar destruction, dermatitis, nasal irritation, and hypersensitivity (Somaye et al., 2019).

Table 4.7: Mean concentrations (mg/kg) of heavy metals compared with acceptable limits of regulatory bodies.

Cosmetics	Pb	Cd	As	Fe	Ni	Cr	Hg
Local							
Lotion	0.43±0.51	0.88±0.38	10.05±0.29	1.50±0.58	BDL	0.41±0.35	6.24±0.20
Cream	1.57±0.81	3.16±2.05	1.25±0.65	0.04±0.00	BDL	0.33±0.21	8.25±1.96
Eyeliner	1.22±1.03	2.00±1.77	9.23±0.19	6.85±2.54	BDL	1.39±0.37	0.26±0.13
Lipstick	5.69±3.85	2.49±1.56	3.62±1.98	9.87±5.23	0.01±0.00	7.26±4.96	BDL
Imported							
Lotion	8.71±5.17	5.55±3.80	5.72±0.99	7.11±3.35	0.01±0.00	7.68±3.67	1.63±0.76
Cream	6.19±3.37	3.69±1.90	3.38±3.90	2.51±2.43	0.02±0.01	5.05±1.83	5.03±1.64
Eyeliner	9.05±4.65	4.56±2.31	4.92±2.78	5.07±3.50	BDL	4.94±0.88	1.84±0.35
Lipstick	13.03±2.00	9.58±1.25	8.11±0.99	12.98±6.12	BDL	5.56±1.49	BDL
Regulatory bodies							
EU	0.5	0.5	-	-	-	1.0	- (EU, 2001)
WHO	10	0.3	-	-	-	-	1.0 (WHO, 2010)
USFDA	20.0	-	3.0	-	-	-	1.0(USFDA, 2000)

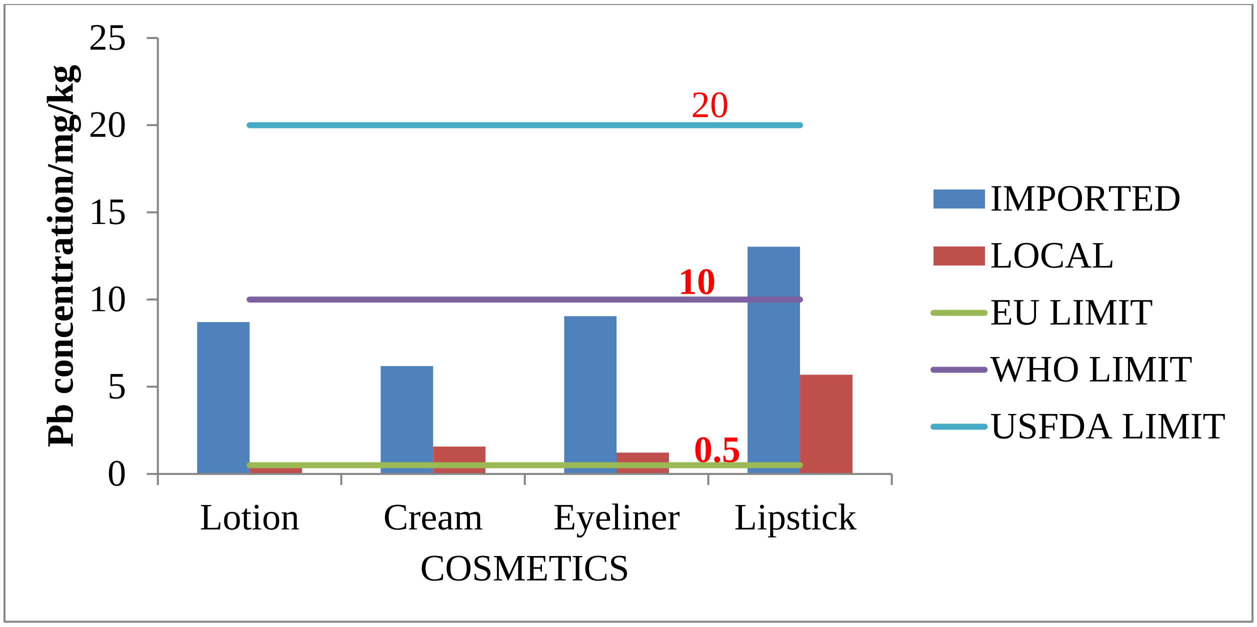

Figure 4.8: Comparing Pb concentration with EU, WHO and USFDA limits

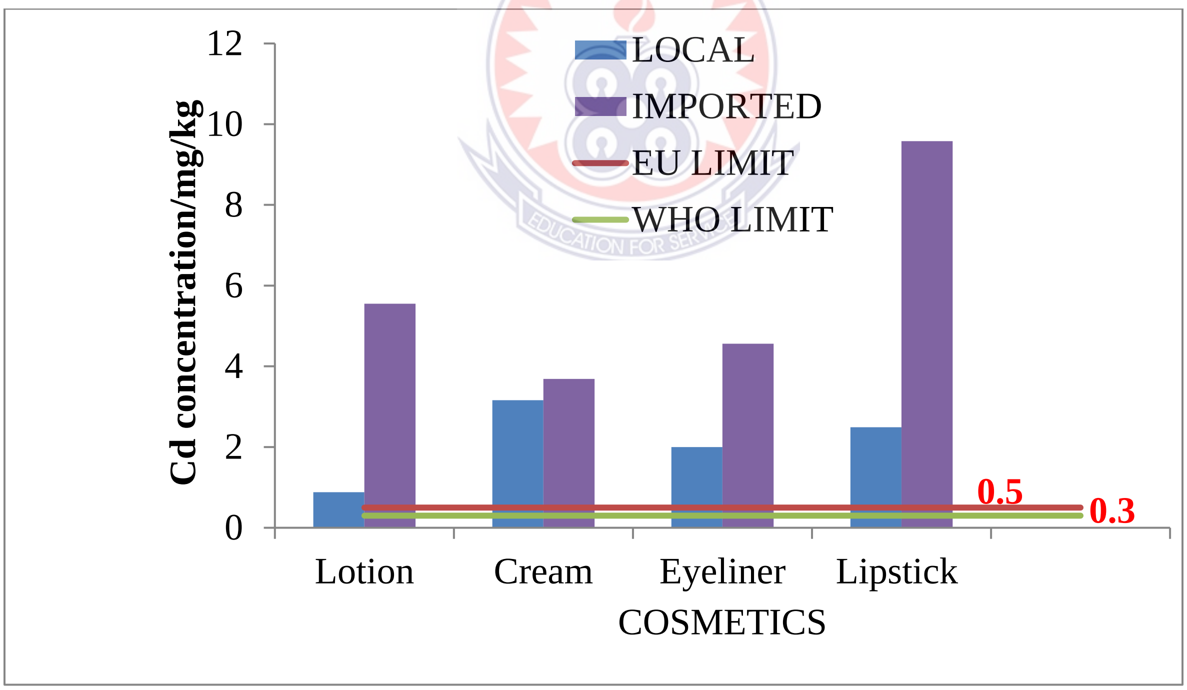

Figure 4.9: Comparing the Cd concentration with EU and WHO limits

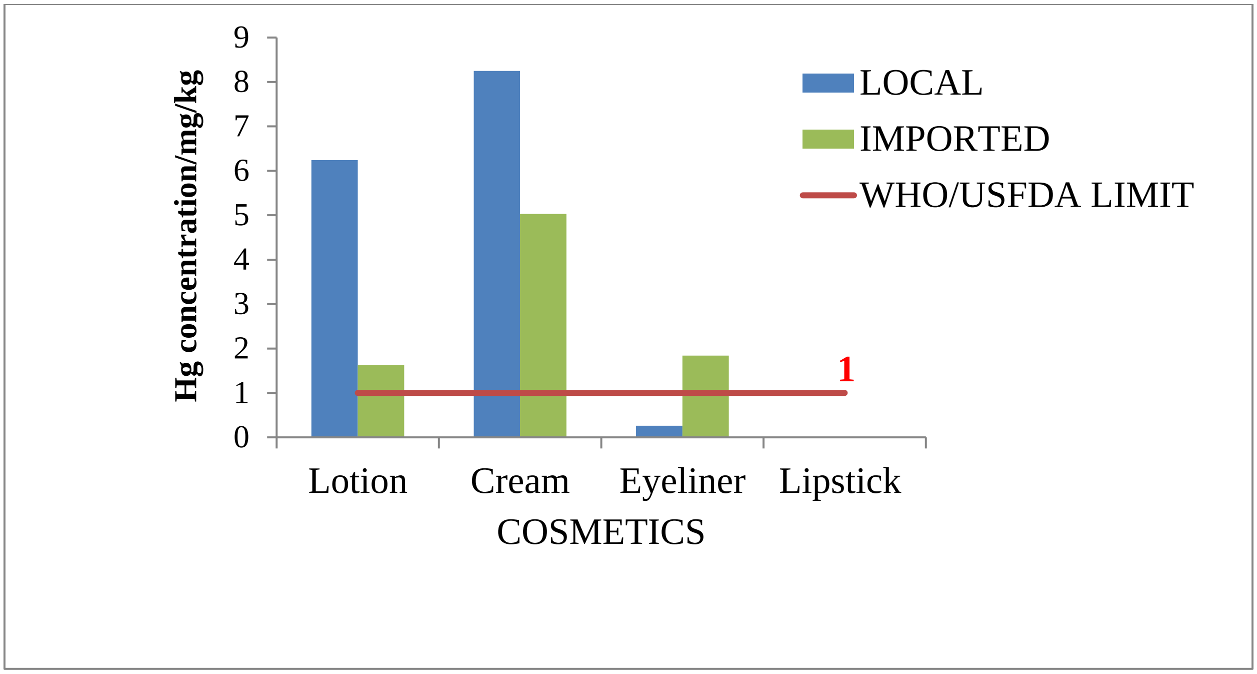

Figure 4.10: Comparing Hg concentration with WHO and USFDA limit.

4.5 Health risk assessment

4.5.1 Margin of Safety (MoS)

The margin of safety index was computed to assess the risk of human contact with metallic impurities in cosmetic products. The margin of safety level for the heavy metals was estimated and presented in Table 4.7. According to World Health Organization (WHO), for a cosmetic to be safe for use, the MoS should be greater than 100. However, the MoS for all the metals in the cosmetics sample were below the WHO standard (100). This implies both local and imported cosmetics samples were not safe and therefore can pose dangerous health risks to consumers. Additionally, these results underscore a critical public health problem since diverse people especially the youth patronize cosmetics products daily. The highest MoS index was 1.68×10^{0} and recorded by a local lotion for Pb while the lowest MoS value was 4.26×10^{-9} for Ni. Besides, the MoS values of this study were inconsistent with those reported by Ghaderpoori et al. (2019) and Usman et al. (Ghaderpoori et al., 2019, Usman et al., 2021). Moreover, Arshad et al. (2020) reported that in lotion cosmetics, the MoS values for Cd, Cr, and Pb were greater than 100 (Arshad et al., 2020). The findings of Arshad et al. (2020) are in agreement with the findings of this study.

Table 4.8: Margin of Safety for heavy metal(loid)s

Cosmetic	Pd	Cd	As	Fe	Ni	Cr	Hg
Local							
Lotion	1.68×10^{0}	2.34×10^{-5}	6.17×10^{-5}	4.83×10^{-3}	-	1.51×10^{-4}	9.44×10^{-4}
Cream	4.60×10^{-1}	6.54×10^{-4}	4.95×10^{-4}	1.81×10^{-5}	-	1.88×10^{-4}	7.13×10^{-4}
Eyeliner	1.04×10^{-8}	1.82×10^{-7}	1.19×10^{-8}	1.86×10^{-7}	-	7.86×10^{-9}	3.99×10^{-8}
Lipstick	1.31×10^{-6}	8.58×10^{-7}	1.77×10^{-7}	7.56×10^{-7}	4.26×10^{-9}	8.81×10^{-7}	-
Imported							
Lotion	8.00×10^{-2}	3.99×10^{-4}	1.08×10^{-4}	1.02×10^{-3}	4.13×10^{-6}	8.06×10^{-4}	3.61×10^{-3}
Cream	1.20×10^{-1}	6.13×10^{-4}	1.83×10^{-4}	2.88×10^{-3}	2.06×10^{-4}	1.23×10^{-3}	1.17×10^{-3}
Eyeliner	1.41×10^{-7}	7.84×10^{-8}	2.22×10^{-8}	2.52×10^{-7}	-	2.21×10^{-7}	5.64×10^{-7}
Lipstick	5.74×10^{-5}	2.23×10^{-7}	7.88×10^{-8}	5.74×10^{-5}	-	1.15×10^{-6}	-

4.5.2 Non-carcinogenic risks

The hazard quotient (HQ) was determined to assess the non-carcinogenic risk of the heavy metals in the cosmetic samples. When the HQ > 1, the exposed population will experience adverse health risks. Table 4.8 depicted that most of the HQ values for almost all the metals except Ni in the cosmetic samples were greater than 1. This means that there is a health risk associated with the cosmetic samples. For the local cosmetics, the HQ value of As in lotion was the highest, and the lowest HQ value was found in Ni in lipstick (Table 4.9). In the imported cosmetics, the highest HQ value was observed in Fe for lotion samples as 9.84×10^{3} and the lowest HQ value of 1.77×10^{-2} was found in Hg in eyeliner. If the hazard index (HI) > 1, it implies that the exposed consumer is at risk. Figure 4.8, showed that both local and imported cosmetics have HI values greater than 1, interpreting that the cosmetic samples are a threat to human health. The highest HI value (2.43×10^{4}) was found in imported lotion whiles the least HI value (1.11×10^{0}) was observed in imported eyeliner. On the contrary, Alam et al. (2019) and Ghaderpoori et al. (2019) reported HI values which were less than 1.

Table 4.9: Hazard Quotient (HQ) and Hazard Index (HI) of heavy metal(loid)s in cosmetics

Cosmetic	**HQ values**							**HI values**
	Pb	**Cd**	**As**	**Fe**	**Ni**	**Cr**	**Hg**	
Local								
Lotion	5.94×10^{1}	4.26×10^{2}	1.62×10^{4}	2.07×10^{3}	-	6.62×10^{1}	1.06×10^{3}	1.99×10^{4}
Cream	2.17×10^{2}	1.53×10^{3}	2.02×10^{3}	5.53×10^{1}	-	5.32×10^{1}	1.40×10^{3}	5.28×10^{3}
Eyeliner	9.56×10^{-3}	5.50×10^{-2}	8.43×10^{-1}	5.40×10^{-1}	-	1.30×10^{-2}	2.51×10^{-3}	1.46×10^{0}
Lipstick	7.6. ×10^{-1}	1.17×10^{0}	5.65×10^{0}	1.32×10^{1}	2.35×10^{-4}	1.14×10^{0}	-	2.19×10^{1}
Imported								
Lotion	1.21×10^{3}	2.51×10^{3}	9.23×10^{3}	9.84×10^{3}	2.40×10^{-1}	1.24×10^{3}	2.77×10^{2}	2.43×10^{4}
Cream	8.56×10^{2}	1.63×10^{3}	5.45×10^{3}	3.47×10^{3}	4.90×10^{-1}	8.15×10^{2}	8.54×10^{2}	1.31×10^{4}
Eyeliner	7.00×10^{-2}	1.30×10^{-1}	4.50×10^{-1}	3.97×10^{-1}	-	4.50×10^{-2}	1.77×10^{-2}	1.11×10^{0}
Lipstick	1.74×10^{0}	4.49×10^{0}	1.27×10^{1}	1.74×10^{1}	-	8.70×10^{-1}	-	3.72×10^{1}

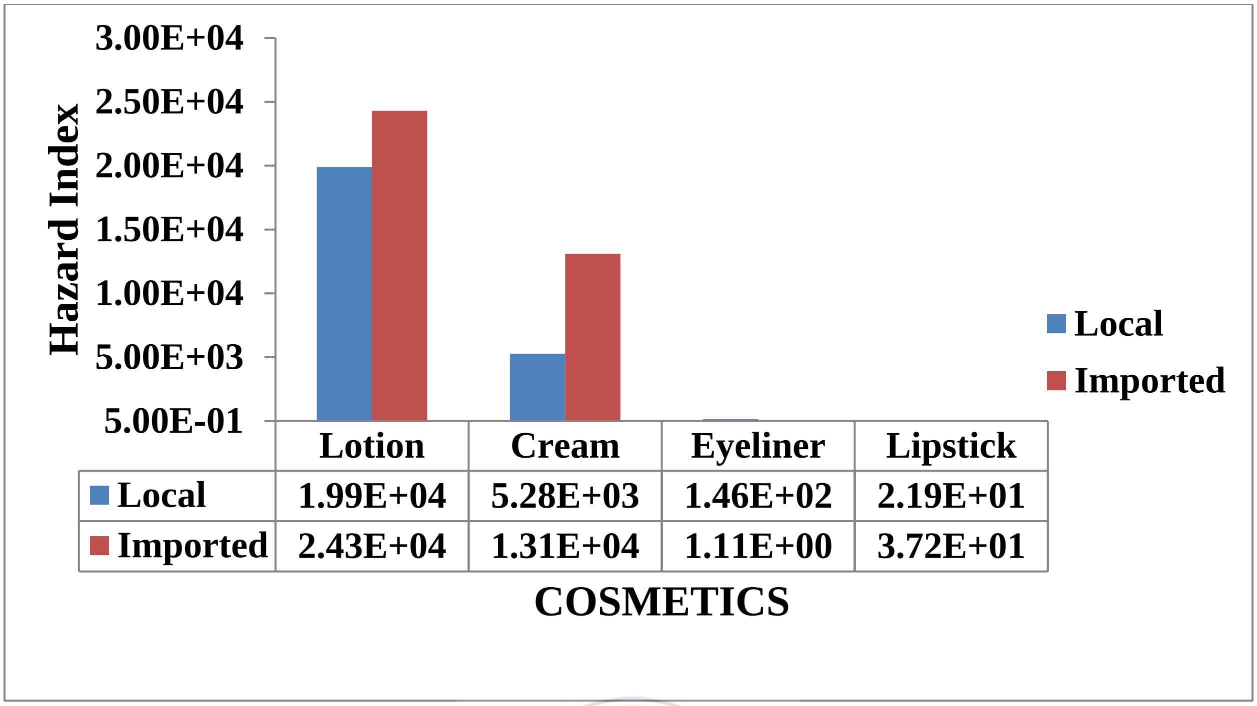

Figure 4.11: Non-carcinogenic risk of heavy metal(loid)s in cosmetics.

4.5.3 Carcinogenic Risks

Due to the unavailability of dermal slope factor for Pb, Ni, Fe, Cd, and Hg, this study only estimated the carcinogenic risk of two metals (Cr and As) in the cosmetic samples. Dermal and ingestion are the main routes through which metals can enter the body. The non-biodegradable nature of heavy metals enables them to remain in the body for a very long period and hence can alter the functions of the body cells and also affect intracellular mechanisms (Arshad et al., 2020). Cancer risk (CR) is an estimation of potential cancer risk to the exposed user of the heavy metals in the cosmetic samples. According to Zheng et al. (2020) the tolerance CR value range from 1×10^{-6} to 1×10^{-4}. From Table 4.10, the CR of Cr for local and imported cream was 6.70×10^{-2} and 1.03×10^{0} respectively, which are all higher than the tolerance level. The same trend of results for CR in Cr was repeated for imported lotion samples. For As in both lotions and cream samples, the CR values were above the tolerance level as seen in Table 4.11.

Furthermore, the cream and lotion were selected for the CR estimation because they are applied to a large body area and also in a large amount as compared to lipstick and eyeliner which are applied to a small area and in a small amount. The CR value obtained in this study is consistent with those obtained by Arshad et al. (2020), which were also above the permissible limits.

Table 4.10: Carcinogenic risk of chromium for dermal exposure pathway for body cream and lotion samples

Cosmetics	**SED_{Dermal}**	**Slope factor**	**Cancer Risk (CR)**
Local : cream	3.19×10^{-2}	2.1	6.70×10^{-2}
Imported: cream	4.89×10^{-1}	2.1	1.03×10^{0}
Local: lotion	3.97×10^{-2}	2.1	8.34×10^{-2}
Imported: lotion	7.44×10^{-1}	2.1	1.56×10^{0}

Table 4.11: Carcinogenic risk of Arsenic for dermal exposure pathway for body cream and lotion samples

Cosmetics	**SED_{Dermal}**	**Slope factor**	**Cancer Risk (CR)**
Local : cream	1.21×10^{-1}	47.5	5.75×10^{0}
Imported: cream	3.27×10^{-1}	47.5	1.55×10^{1}
Local : lotion	9.37×10^{-1}	47.5	4.62×10^{1}
Imported: lotion	5.54×10^{-1}	47.5	2.63×10^{1}

4.6 Analysis of VOCs in cosmetics

People have been exposed to elevated levels of VOCs via the use of household substances such as paint, detergents, cosmetics, and personal care products. The exposure of VOCs to consumers through the patronage of cosmetics and personal care products is of great concern since there is a surge in the use of these products among people. The VOCs present in the cosmetic samples analyzed is shown in Table 4.12.

Table 4.12: VOCs present in the cosmetics samples

Samples **Local**	VOCs	R/Time (min)	Samples **Imported**	VOCs	R/ time (min)
Lotion			Lotion		
L1	ND		L4	ND	
L2	Heptadecanoic acid	17.88	L5	ND	
	Pentadecanoic acid	12.78	L6	Undecanoic acid	5.74
L3	5,8,11,14-eicosatetraenoic acid	24.02	Cream		
Cream			C4	ND	
C1	Tridecanoic acid,	8.56	C5	ND	
C2	8,11,14-eicosatrienoic acid	24.57	C6	Undecanoic acid	5.74
C3	Tridecanoic acid	8.56		Sterate acid	20.63
Eyeliner	ND		Eyeliner		
E1	ND		E4	Heptadecanoic acid	17.88
	9-octadecanoic acid	20.00	E5	Cis-11,14-eicosadienoic acid	25.08
E3					
	5,8,11,14- eicosatetraenoic acid	24.06	E6	ND	
Lipstick			Lipstick		
LP1	5,8,11,14- eicosatetraenoic acid	24.08	LP4	5,8,11,14- eicosatetraenoic acid	24.06
			LP5	Pentadecanoic acid	12.80
			LP6	ND	

4.6.1 VOCs in local cosmetics

Several toxic materials are used as vital ingredients during the manufacturing process of cosmetics products. VOCs are compounds present in most household substances including paint, pesticides, cosmetics, and washing agents. In the body lotion, the VOC present in sample L1 is heptadecanoic acid with a retention time of 17.88 min. And also analysis of sample L3 showed pentadecanoic acid and 5,8,11,14-eicosatetraenoic acid with retention time 12.78 min and 24.02 min respectively. However, GC-MS analysis was not able to detect VOC in sample L1 as seen in figure 4.12. The analysis of all three samples of cream; C1, C2, and C3 revealed that Tridecanoic acid, 8, 11, 14-eicosatrienoic acid, and Tridecanoic acid respectively were present. The fatty acids present in cosmetics especially cream helps to control the viscosity and dispersion features of the product. In sample E1 of eyeliner, no VOC was detected by the instrument. The investigation of sample E3 showed VOCs such as 9-octadecanoic acid with a retention time of 20.00 min and 5,8,11,14- eicosatetraenoic acid (RT: 24.06 min). The only lipstick sample, LP1 showed a similar VOC as the eyeliner sample E3.

4.6.2 VOCs in imported cosmetics

Although the Ghanaian markets have locally-made cosmetics and personal care products, most Ghanaians still prefer imported cosmetics to locally made ones because they see locally made ones as being substandard. This has created a situation that most cosmetics shops are dominated by imported cosmetic products. In the analysis of body lotion samples, L4 and L5, the GC-MS detected no VOCs in the samples. In contrast, sample L6 showed undecanoic acid, with a retention time of 5.74 min. The GC-MS analysis could not detect any VOCs present in cream samples C4 and C5. However, sample C6 showed undecanoic acid, and sterate acid with retention times of 5.74 min and 20.63 min respectively. In the eyeliner samples, E4 and E5 showed heptadecanoic acid and cis-11, 14-eicosadienoic acid respectively. The retention time for heptadecanoic acid and cis-11, 14-eicosadienoic acid is 17.88 min and 25.08 min respectively. No VOC was detected in sample E6 (Figure 4.9). The analysis of lipstick sample LP4 revealed that 5, 8, 11, 14- eicosatetraenoic acid (RT: 24.06 min) was present. Also, the sample LP5 showed the VOC pentadecanoic acid (RT: 25.08 min). Nevertheless, the GC-MS analysis could not detect any VOC in sample LP6.

Generally, the analysis of the cosmetics showed that 9 different VOCs are present in the samples. The local samples have VOCs including heptadecanoic acid, pentadecanoic acid, 5, 8, 11, 14-eicosatetraenoic acid, Tridecanoic acid and 9-octadecanoic acid. Whereas, the imported cosmetic samples have VOCs such as undecanoic acid, sterate acid, heptadecanoic acid, cis-11, 14-eicosadienoic acid, and pentadecanoic acid. Moreover, according to the results, samples C6, E3 and L3 have more than one VOCs. The most common VOC which was found in 4 samples (LP1, LP4, L3, E3) is 5, 8, 11, 14-eicosatetraenoic acid.

Furthermore, the result of the study suggests that the VOCs found in the cosmetic samples are predominantly carboxylic acids. These results are in contrast to the findings of Azeez et al. (2013). Azeez et al. (2013) analyzed VOCs in local cosmetics in Nigeria and the results showed VOCs such as formaldehyde, toluene, trichloroethene, and tetrachloroethene were found (Azeez et al., 2013). Gherghel and co-workers investigated VOCs in cosmetics such as lipstick, face cream, and aftershave lotion manufactured in south India and the results showed the VOCs present are 14-Methylpentadecanoic acid methyl ester, Palmitic acid methyl ester, and 10-Octadecanoic acid methyl ester (Gherghel et al., 2018). The study results are consistent with the results of Gherghel and co-workers. Nilsson et al. (2005) examined VOCs in dust from textile surfaces and the results found alkanes, alcohols, and carboxylic acids (Nilsson et al., 2005). There is a clear similarity between the results of this study and the findings of Nilsson and co-workers, despite the differences in the type of samples. Moreover, Vu and co-workers revealed that aldehydes such as nonanal, decanal, benzaldehyde, and octanal are commonly used as odorants in flavors, perfumes, and cosmetics products (Vu et al., 2018). The analysis of the cosmetic sample did not detect any aldehyde as part of the VOCs present and this could be a result of the sample preparation technique employed.

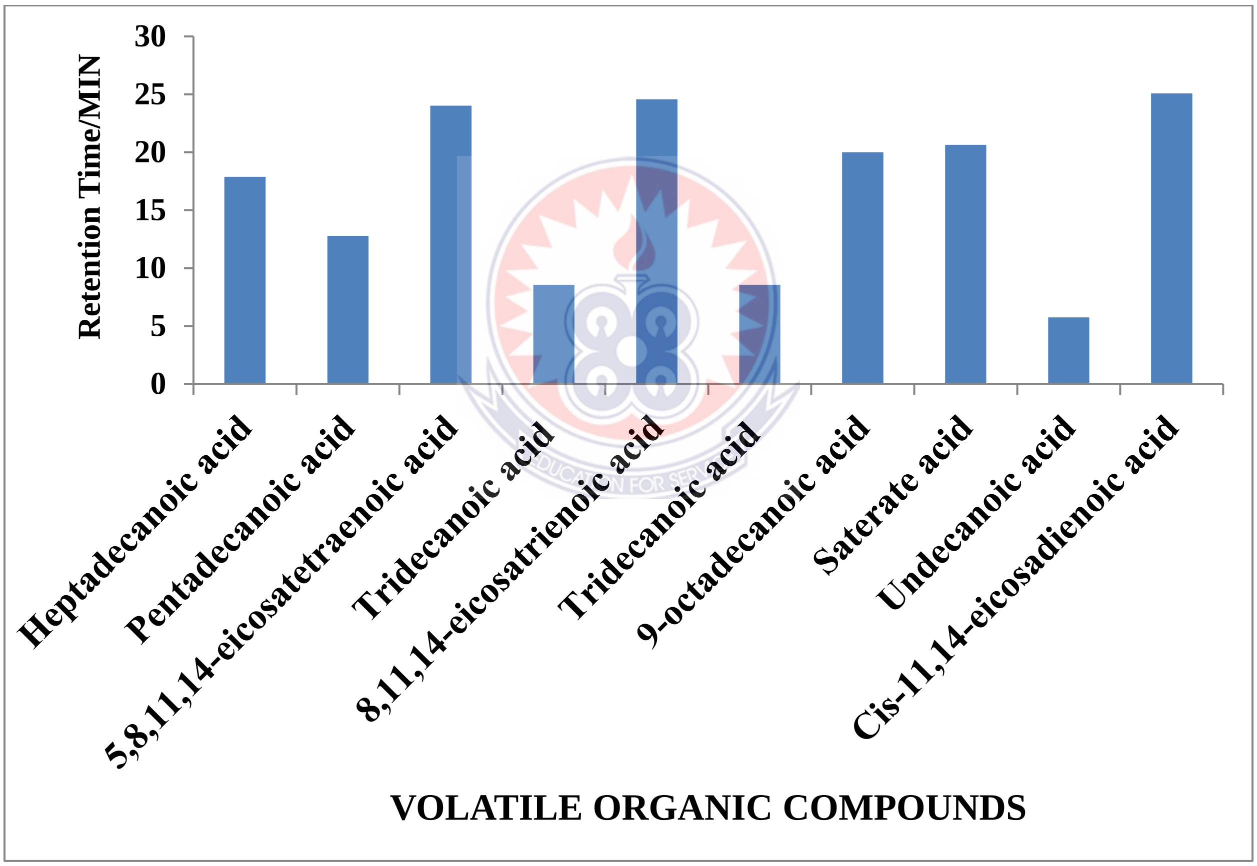

Figure 4.12: Volatile organic compounds versus their retention times

CHAPTER FIVE

5.0 SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

5.1 Summary of findings

- The concentrations of the metals in imported cosmetics were generally higher than the metal concentrations in local cosmetics and this may be as a result of inadequate quality control measures taken by the foreign manufacturing companies.
- The concentrations of metals such as Pb, Fe and Cr were higher in coloring cosmetics including lipstick and eyeliner since they are utilized as coloring agents during the manufacturing process.
- The metals present in both cosmetic products may come from metallic containers used in packaging the cosmetic products.
- The levels of Ni in both cosmetic products were very low.
- The cosmetic products may also be contaminated with heavy metals during transportation since heavy metals are ubiquitous.
- The VOCs present in the cosmetic products may be introduced during the preparation of the cosmetics products.
- All the VOCs in the cosmetic products contain carboxylic acid functional group.

5.2 Conclusion

The study was carried out to determine the concentrations of heavy metals in both local and imported cosmetics. Seven metals were analyzed in 21 cosmetic samples collected from the Kejetia Market in the Ashanti region. The seven metal(loid)s assessed include Pb, Cd, As, Fe, Ni, Cr, and Hg.

According to the results, concentrations of some of the metals in imported cosmetic samples were higher than those found in local cosmetic samples. However, there was no significant difference between the concentrations of the metals in both local and imported cosmetic samples. Also, the MoS values for all the metals in the cosmetics sample were below the WHO standard of 100. This implies both local and imported cosmetics samples were not safe and therefore can pose adverse health risks to consumers. The HQ and HI values for almost all the metals in the cosmetic samples were greater than their permissible limits (<1.0), meaning that there is a health risk associated with the cosmetic samples. On the other hand, CR for Cr and As in local and imported cream and lotion were all higher than the tolerance levels. Moreover, the concentrations of some of the metals in the cosmetic products that the regulatory bodies have set a threshold for were observed to be higher than the acceptable permissible limits.

Furthermore, the analysis of the cosmetics samples showed that 9 different VOCs are present in the samples. The local samples have VOCs including heptadecanoic acid, pentadecanoic acid, 5, 8, 11, 14-eicosatetraenoic acid, Tridecanoic acid and 9-octadecanoic acid. Whereas, the imported cosmetic samples have VOCs such as undecanoic acid, sterate acid, heptadecanoic acid, cis-11, 14-eicosadienoic acid, and pentadecanoic acid.

5.3 Recommendations

Based on the outcomes of the study, the following recommendations have been made.

1. Ghana Food and Drugs Authority (FDA) and Ghana Standard Authority (GSA) should;
   - Monitor heavy metals and VOCs content in both imported and local cosmetic products on the Ghanaian markets and where it is appropriate sanctions should be applied.
   - Conduct public awareness education on the dangers of using cosmetics that contain heavy metals and VOCs.
2. Cosmetics manufacturing companies should conduct adequate quality control checks on the raw materials they used to manufacture cosmetics since some of the metals may originate from the starting materials.
3. The study recommends further research should be conducted on other cosmetic products apart from those used in this study to assess the heavy metal and VOCs levels in them.
4. Advice users of cosmetic products to reduce or avoid if possible until a standard guideline for acceptable limits of potential contaminants in cosmetics is adequately addressed.

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APPENDIX A

Ghana Atomic Energy Commission

Department of chemistry

Analysis of heavy metal(loid)s in cosmetics

Concentrations (mg/kg) of heavy metals in cosmetics samples

Experiment 1

Sample ID	Pb	Cd	As	Fe	Ni	Cr	Hg
L1	0.231	1.245	0.562	ND	ND	0.089	0.045
L2	0.059	0.897	0.023	ND	ND	0.784	0.012
L3	1.012	0.487	0.090	ND	ND	0.362	0.008
C1	2.365	3.879	0.789	0.008	0.001	0.564	0.125
C2	1.598	4.752	1.984	0.015	0.004	0.258	0.096
C3	0.741	0.852	0.963	0.085	0.009	0.159	0.084
E1	0.489	3.256	0.074	0.071	0.002	1.126	0.357
E3	1.951	0.756	0.348	0.068	0.003	1.648	0.169
LP1	5.692	2.489	3.621	9.874	0.005	7.256	ND
L4	10.231	6.567	4.963	8.854	0.006	6.654	0.756
L5	12.951	8.753	6.856	9.236	0.008	11.741	2.152
L6	2.954	1.357	5.354	3.248	0.010	4.651	1.987
C4	3.465	2.845	1.520	1.105	0.002	6.230	4.589
C5	5.145	2.365	0.756	1.117	0.009	2.950	6.852
C6	9.952	5.874	7.861	5.320	0.008	5.980	3.654
E4	15.845	5.956	6.254	6.842	0.004	4.631	2.150
E5	2.547	1.893	1.728	1.028	0.006	5.932	1.457
E6	8.756	5.834	6.786	7.325	0.001	4.245	1.927
LP4	14.643	8.750	9.258	10.760	0.002	6.235	ND
LP5	13.682	11.012	7.563	8.651	0.008	6.602	ND
LP6	10.789	8.965	7.512	8.950	0.007	3.856	ND

Experimental 2

Sample ID	Pb	Cd	As	Fe	Ni	Cr	Hg
L1	0.232	1.127	0.685	ND	ND	0.090	0.030
L2	0.056	0.826	0.024	ND	ND	0.821	0.011
L3	1.012	0.389	0.092	ND	ND	0.423	0.007
C1	2.345	3.765	0.765	0.006	0.002	0.478	0.125
C2	1.598	4.012	2.147	0.014	0.003	0.361	0.010
C3	0.785	0.852	0.960	0.080	0.010	0.245	0.084
E1	0.345	3.125	0.065	0.065	0.003	1.012	0.356
E3	1.862	0.756	0.312	0.075	0.003	1.589	0.170
LP1	4.231	2.578	3.564	9.860	0.004	7.225	ND
L4	10.231	6.567	4.963	8.678	0.007	6.671	0.756
L5	11.568	8.685	6.789	9.236	0.009	11.658	2.153
L6	1.998	1.258	5.350	3.241	0.010	4.650	1.987
C4	3.465	2.562	1.520	1.113	0.001	6.445	4.589
C5	5.145	2.456	0.752	1.107	0.010	3.012	6.852
C6	9.952	5.985	7.812	5.331	0.008	5.980	3.655
E4	15.784	5.956	6.254	6.842	0.005	4.642	2.151
E5	2.547	1.869	1.365	1.042	0.005	5.913	1.456
E6	8.756	5.752	6.786	7.324	0.002	4.230	1.927
LP4	14.643	8.750	9.248	10.761	0.003	6.235	ND
LP5	13.682	11.000	7.523	8.644	0.008	6.611	ND
LP6	9.998	8.975	7.650	8.965	0.007	3.856	ND

Experimental 3

Sample ID	Pb	Cd	As	Fe	Ni	Cr	Hg
L1	0.232	1.245	0.560	ND	ND	0.091	0.045
L2	0.058	0.890	0.024	ND	ND	0.875	0.012
L3	1.011	0.488	0.091	ND	ND	0.465	0.007
C1	2.366	3.880	0.790	0.008	0.002	0.512	0.124
C2	1.580	4.762	1.985	0.015	0.005	0.250	0.097
C3	0.742	0.851	0.963	0.085	0.009	0.159	0.085
E1	0.490	3.254	0.074	0.071	0.006	1.126	0.430
E3	1.962	0.753	0.349	0.068	0.004	1.647	0.173
LP1	5.692	2.489	3.623	9.874	0.005	7.253	ND
L4	10.242	6.567	4.963	8.854	0.006	6.653	0.712
L5	13.012	8.750	6.857	9.236	0.008	11.750	2.136
L6	2.960	1.358	5.354	3.248	0.009	4.661	1.987
C4	3.456	2.845	1.522	1.105	0.003	6.223	4.589
C5	5.152	2.366	0.756	1.117	0.010	2.942	6.782
C6	10.012	5.874	7.863	5.320	0.009	6.854	3.654
E4	15.825	5.957	6.255	6.842	0.004	4.642	2.150
E5	2.556	1.892	1.724	1.028	0.005	5.932	1.454
E6	8.756	5.834	6.780	7.325	0.002	4.223	1.926
LP4	14.645	8.751	9.258	10.760	0.003	6.458	ND
LP5	13.680	11.013	7.564	8.651	0.007	6.600	ND
LP6	10.790	8.965	7.513	8.950	0.008	3.887	ND

Kuskal-Wallis Test

Ranks

	cosmetics	N	Mean Rank
pb	L-Lotion	1	1.00
	L-Cream	1	3.00
	L-Eyeliner	1	2.00
	L-Lipstick	1	4.00
	I-Lotion	1	6.00
	I-Cream	1	5.00
	I-Eyeliner	1	7.00
	I-Lipstick	1	8.00
	Total	8	
Cd	L-Lotion	1	1.00
	L-Cream	1	4.00
	L-Eyeliner	1	2.00
	L-Lipstick	1	3.00
	I-Lotion	1	7.00
	I-Cream	1	5.00
	I-Eyeliner	1	6.00
	I-Lipstick	1	8.00
	Total	8	
As	L-Lotion	1	8.00
	L-Cream	1	1.00
	L-Eyeliner	1	7.00
	L-Lipstick	1	3.00
	I-Lotion	1	5.00
	I-Cream	1	2.00
	I-Eyeliner	1	4.00
	I-Lipstick	1	6.00
	Total	8	
Fe	L-Lotion	1	2.00
	L-Cream	1	1.00
	L-Eyeliner	1	5.00
	L-Lipstick	1	7.00
	I-Lotion	1	6.00
	I-Cream	1	3.00

Ranks

	cosmetics	N	Mean Rank
Fe	I-Eyeliner	1	4.00

Ranks

	cosmetics	N	Mean Rank
Fe	I-Eyeliner	1	4.00
	I-Lipstick	1	8.00
	Total	8	
Ni	L-Cream	1	2.50
	L-Eyeliner	1	2.50
	L-Lipstick	1	5.50
	I-Lotion	1	5.50
	I-Cream	1	7.00
	I-Eyeliner	1	2.50
	I-Lipstick	1	2.50
	Total	7	
Cr	L-Lotion	1	2.00
	L-Cream	1	1.00
	L-Eyeliner	1	3.00
	L-Lipstick	1	7.00
	I-Lotion	1	8.00
	I-Cream	1	5.00
	I-Eyeliner	1	4.00
	I-Lipstick	1	6.00
	Total	8	
Hg	L-Lotion	1	5.00
	L-Cream	1	6.00
	L-Eyeliner	1	1.00
	I-Lotion	1	2.00
	I-Cream	1	4.00
	I-Eyeliner	1	3.00
	Total	6	

Test Statistics[a,b]

	pb	Cd	As	Fe	Ni	Cr	Hg
Chi-Square	7.000	7.000	7.000	7.000	6.000	7.000	5.000
Df	7	7	7	7	6	7	5
Asymp. Sig.	.429	.429	.429	.429	.423	.429	.416

a. Kruskal Wallis Test
b. Grouping Variable: cosmetics