MASS SPECTROMETRIC QUANTIFICATION AND HEALTH RISK ASSESSMENT OF HEAVY METALS IN LIPSTICK AND EYE SHADOW PRODUCTS IN MOMBASA COUNTY, KENYA

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U59/11785/2018

A thesis submitted in partial fulfillment of the requirements for the award of the Degree of

Master of Pharmacy in Pharmaceutical Analysis of the University of Nairobi

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Assessment of Heavy Metals in Lipstick and Eye Shadow

Products in Mombasa County, Kenya

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ACKNOWLEDGMENTS

I am indebted to my supervisors whose motivation and guidance helped me to complete this work. Invaluable appreciation goes to Dr. Alex Okaru, Dr. Dennis Ongarora, and Dr. Stanley Ndwigah, for their unwavering support, mentorship, and acting as fatherly figures throughout this research.

I also acknowledge all my lecturers and non-teaching staff in the Department of Pharmaceutical Chemistry, Pharmaceutics and Pharmacognosy in the Faculty of Health Sciences of the University of Nairobi who equipped me with skills, and knowledge, and mentored me towards academic excellence.

Moreover, I am extremely thankful to the staff at the analytical chemistry laboratory of Kenya Plant Health Inspectorate Services (KEPHIS) Nairobi, for the excellent technical assistance and good cooperation during the design and execution of experiments regarding the analysis of heavy metals in cosmetics using Inductively Coupled Plasma-Mass Spectrophotometer (ICP-MS).

DEDICATION

Special thanks to my beloved family for always believing in me and for encouraging me to strive for my dreams.

Also my mentors, friends, and college mates shared their words of advice and encouragement to enable me to finish this study.

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LIST OF ABBREVIATIONS AND ACRONYMS

AAS Atomic Absorption Spectroscopy

AES Atomic Emission Spectroscopy

ATSDR Agency for Toxic Substance and Disease Registry

CDI Chronic Daily Intake

CR Cancer Risk

EAC East African Community

EU European Union

FDA Food and Drug Administration

HI Hazard Index

HQ Hazard Quotient

IARC International Agency for Research on Cancer

ICP-MS Inductively Coupled Plasma Mass Spectrometry

KEBS Kenya Bureau Of Standards

KEPHIS Kenya Plant Health Inspectorate Services

PCP Personal Care Products

PPM Parts Per Million

SADC South African Development Community

US EPA United States Environmental Protection Agency

WHO World Health Organization

SYMBOLS OF ELEMENTS

Symbol	Element				

As Arsenic

Cd Cadmium

Co Cobalt

Cr Chromium

Ga Gallium

Ge Germanium

Hg Mercury

Mn Manganese

Ni Nickel

Pb Lead

Sb Antimony

Tl Thallium

DEFINITION OF OPERATIONAL TERMS

Carcinogen: An agent capable of causing cancer in living tissue (1).

Cosmetic: This is a chemical preparation applied to the body, to improve its

appearance (2).

Health risk: This is a characteristic or exposure of an individual that increases the

likelihood of developing a disease (3).

Heavy metals: These are metals of relatively high density usually five times greater than

that of water and considered toxic to humans at low concentrations (3).

Risk assessment: This is a screening tool that identifies and understands health risk status over

time (4).

ABSTRACT

Heavy metal presence in lipsticks and eye shadows is of public health concern since the contamination poses potential health risks and environmental pollution. Some of the deleterious effects of these metals include damage to the brain, kidneys and bone marrow. This study sought to determine metal content and their associated risk in commonly used lipstick and eye shadow products in Mombasa County.

Seventy-nine (79) samples of lipsticks and eye-shadows were purchased from different cosmetic shops and open markets in the four sub-counties of Mombasa County. Determination of metal content was done with Inductively Coupled Plasma Mass Spectrometer. Risk assessment was evaluated using margin of safety, hazard quotient, hazard index, and carcinogenic risk approach for both carcinogenic and non-carcinogenic effects.

Six metals, namely arsenic, chromium, lead, cadmium, mercury and cobalt were determined in samples comprising 58 lipsticks and 21 eye shadows using ICP-MS. The concentration of some of the metals was much higher in the samples than the recommended maximum acceptable limit. The mean of As, Cr, Pb, Cd, Hg, and Co in lipsticks was 1.24±0.83, 6.69±23.99, 4.43±5.15, 0.05±0.19, 0.47±0.43, and 0.82±0.87 ppm, respectively, and in eye shadows 1.27±0.64, 17.28±35.06, 8.10±10.56, 0.08±0.38, 0.34±0.41, and 0.85±0.95 ppm, respectively.

The order of mean concentrations was Cr > Pb > As > Co > Hg > Cd. Heavy metals concentration in some samples was above the World Health Organization (WHO) suggested safe limits.

Based on the results, these products are contaminated with one or more metals with hazard quotient and hazard index being less than unity. Hence these cosmetics are generally safe to use. However, continuous use can increase the absorption into the human body which is harmful to health.

The presence of metals such as mercury and lead in the sampled cosmetics necessitates strict regulatory monitoring to protect consumers. Continuous postmarketing surveillance on cosmetics is also recommended.

CHAPTER ONE: INTRODUCTION

1.1 Background

Lipsticks and eye shadows are some of the personal care products (PCPs) widely used (5,6), either for body cleansing or beautification purposes (7). PCPs have been used for several centuries, to alter appearance and are perceived to promote attractiveness (8). Other PCPs include lip balm, lip gloss, beauty soap, makeup, henna, shampoo, facial cream and anti-aging cream among others.

Lipsticks come in varying colors and are made up of pigments and emollients. The pigments impart color while emollients hydrate the lips. Similar to pharmaceutical products, beauty products may contain impurities such as heavy metals and microbial contaminants. Heavy metal impurities in cosmetics are poisonous (3,9) since these metals are gradually absorbed over time and accumulate in the body tissues or organs (10).

Heavy metals are considered environmental pollutants and produce toxicity when interacting with biological systems (3,11). On accumulation to toxic levels, these metals are harmful to human health. Metal poisoning may be due to industrial exposure, air pollution, water contamination, food contamination, or dermal contact when applying cosmetics on the body (12,13).

Some of the metals that may end up in the final products as impurities are lead, mercury, cadmium, arsenic, manganese, chromium, cobalt, thallium, nickel, and zinc. These metals occur naturally in soil, water, and environment (3). The metals persist in the environment as they cannot be degraded and hence may have a cumulative effect (3,14).

1.2 Heavy metals of potential public health significance

Metals classified as micronutrients such as cobalt, manganese, copper, zinc, and selenium are essential elements in maintaining body metabolism but are toxic at a concentration exceeding a certain threshold (14,15). Medicinal metals find their use in pharmaceuticals and include platinum (anticancer) and gold (arthritis). Other metals such as thallium and gallium are used as radionuclides in single photon emission computerized tomography (SPECT) that aid in the diagnosis of cancer.

Metals associated with toxicity in humans are found in cosmetics especially lipstick and eye shadow (16,17). Examples are lead, arsenic, mercury, cadmium, nickel, chromium, and manganese. These metals are of public health concern and among the top ten on the hazardous chemical list of the ATSDR (18).

1.2. 1 Lead

Lead (Pb) is a group IVa element with an atomic number and a mass of 82 and 207, respectively. This metal is not commonly found in the earth's crust but it is readily available and is chiefly used in lead-acid storage batteries. Lead is a common impurity in PCPs and has been identified as among the sources of metal toxicity (19,20). According to the research by Health Metrics and Evaluation Institute, lead poisoning is a significant cause of mortality and morbidity (21).

Lead causes toxic effects on the reproductive, hematopoietic, nervous, renal, and cardiovascular systems (13). As a result of lead toxicity, anemia, colic, neuropathy, behavioral and learning impairment, and impaired cognitive function can occur (13). Lead toxicity mode of action is not fully elaborated in studies but the prime target leading to lead toxicity are antioxidants and heme synthesis (22).

1.2.2 Arsenic

Arsenic (As) with a mass of 74.92 and an atomic number of 33, is a metalloid found in group IV of the periodic table. Arsenic exists as iron arsenide sulfide in the earth's deposits and in the atmosphere as arsenic trioxide (23). The toxic form of arsenic is inorganic arsenic trichloride. Chronic exposure to arsenic and its compounds can cause skin lesions and other health effects such as skin cancer (24).

Arsenic toxicity in the biological system can cause cell injury through multi mechanisms such as interference with cellular respiration. The metabolism of arsenic to a trivalent state and oxidative methylation to a pentavalent state. The inorganic arsenic may replace phosphate in several reactions (25,26).

1.2.3 Mercury

Mercury with an atomic number of 80 and a mass of 200.59, occurs naturally and is toxic to human beings. With a very low melting point and a high boiling point, mercury is liquid at room temperature. The metal can be obtained commercially from a mercuric sulfide ore and is easily separated by melting the ore in the air. This metal is an ingredient found in skin-lightening creams and soaps (27). Mercury toxicity affects vital organs including the skin and the eyes (28).

The mechanism of mercury toxicity in humans is due to the methylation of mercury to form methylmercury hence production of reactive oxygen and disrupting calcium homeostasis (25).

1.2.4 Cadmium

Cadmium (Cd) is found in the d-block and has an atomic number and a mass of 48 and 112.4, respectively. The salts of cadmium include; cadmium sulfide, cadmium carbonate, and cadmium

oxide, with the sulfide being the main source of cadmium. The principal target of cadmium toxicity is the kidneys and bones (Elinder & Traub, 2019).

Chromosome deletions and mutations are brought on by cadmium. Its toxicity results from the reduction of reduced glutathione, which increases the generation of reactive oxygen species (25,29).

1.2.5 Manganese

Manganese (Mn) with an atomic number of 25 and a mass of 55 has high melting and boiling points of 1246° and 2061° respectively. Manganese occurs mainly in the form of manganese dioxide and is an essential element but potentially toxic to humans. Persistent exposure to manganese causes neurological deficits in humans characterized by mental difficulties and impairment in motor skills (30).

The mechanisms underlying the toxicity involve endocrinological dysfunction and manganese-mediated changes in intracellular calcium and iron metabolism (25). Acute toxicity with manganese causes an increase in uptake by the pancreas, leading to a sharp reduction in circulating insulin hence an increase in plasma glucose (30).

1.2.6 Chromium

Chromium (Cr) is a group six-element with atomic number and mass of 24 and 52 respectively, found chiefly in the earth's crust. Its oxides, hydrated chrome oxide, and chromium oxide are principally used in the manufacture of PCPs, especially soaps.

Chromium (VI) analogs are toxic and carcinogenic since they are classified into group one elements of the IARC classification. According to the WHO report in the year 2003, skin contact

with chromium was reported to induce skin problems including skin ulcers whereas chronic poisoning can cause damage to the kidney and nerve tissues (31).

Exposure to chromium induces toxicity by a complicated multi-front mode of action involving oxidative stress, epigenetic alterations and mutagenesis (32).

1.3 Regulation of cosmetic products

Cosmetic products in Kenya are regulated under the Food, Drugs, and Chemical Substances Act, Cap 254. Legislation relating to the use of ingredients that can be included in PCPs is clear, but not properly enforced. Generally, there is a deficiency in control of heavy metal content in cosmetics since manufacturers do not provide detailed information about the contents of PCPs. Consumers, as a result, have no way of knowing if a cosmetic product they are using has metals or other ingredients that can have adverse effects on their long-term health (33).

The majority of metals found in cosmetic products are toxic if ingested in high concentrations (12,13). According to Massadeh et al. (2017), international regulatory bodies usually prescribe the highest amounts of metals that should be found in PCPs, and manufacturers have to ensure the concentration of metals contained in their products stays below the minimum levels (34,35).

The maximum limits for heavy metals allowed by KEBS a regulatory board in Kenya, mandated by the government for quality products, to be sold in the country are documented (36). Limits of heavy metal contents as prescribed by the KEBS for arsenic, lead, mercury, and total metal content are 2, 20, 2, and 20 parts per million respectively (36). Metals presence in the final products shall be a result of contamination during processing and not deliberate addition as an ingredient (16,37).

Table 1.1 shows the maximum recommended limits of metals in the final products from (36,38). It can be noted in Table 1.1 that there is variability in limits among countries, regions, and

international bodies. The unique limits may have been informed by local/regional epidemiological studies and different levels of sophistication in analytical technologies adopted in the studies. However, for purposes of international commerce, it would have been better to adopt uniform limits globally.

Table 1. 1: Limits of heavy metal content in different countries and regions

		Amount of heavy metals in parts per million (ppm)							
Metal	WHO	EU	SADC	EAC	USA	Canada	Germany	India	Kenya
Arsenic			5	2	3		0.5	2	2
Cadmium	0.3	0.5	5		0.1	3	0.1		
Chromium		1							
Lead	10	0.5	20	10	1	10	2	20	20
Mercury	1		1	2	1		0.1	2	2
Nickel					0.6				

Table 1.1 is adapted from published literature (36,38).

1.4 Sources of heavy metals in cosmetics

Metals found in cosmetic products may arise from the raw material used hence the need to test for metals and comply with requirements (39). The pigments that are notorious for contamination should comply with safety requirements when used. This means regulatory measures to limit the concentrations of metals should focus on using the right materials, in addition to recommending best practices and processes in manufacturing that can be used for detection and removal (39).

1.5 Carcinogenicity of heavy metals

Carcinogenicity is the ability to cause malignancy in living organisms (40). Some popular metals found in lipstick and eye shadow products have carcinogenic potential. According to the Campaign for Safe Cosmetics (2019), cadmium and chromium which are commonly found in PCPs have carcinogenic potential in the case of long-term exposure (41,42).

The chemicals were categorized by the International Agency for Cancer Research (IARC) into various classes as shown in Table 1.2 (43) whether causing cancer or non-carcinogenic based on scientific proof in human and animal studies (43).

Table 1. 2: Carcinogenic risk of different metals

Group/Class	Description	Examples
1	Carcinogenic to humans	Arsenic and inorganic arsenic compounds
		Cadmium and Cadmium compounds
		Nickel
		Chromium VI compounds
2A	Probably carcinogenic	Inorganic lead compounds
2B	Possibly carcinogenic	Methylmercury
		Elemental Lead
		Cobalt
3	Not classifiable	Mercury and inorganic Mercury compounds
		Organic Lead compounds
		Chromium III compounds
4	Probably non-carcinogenic	N/A

The source of table 1.2 is Internation Agency for Research on Cancer (43)

1.6 Analytical techniques for heavy metals

Several analytical techniques and methods have been used for the analysis of heavy metals (44,45). The analytical sensitivity of the methods used varies with some capable of detecting even trace quantities.

Currently, the most preferred technique in metals analysis is Inductively Coupled Plasma Mass Spectrometry (45). Other useful techniques include Anode Stripping Voltammetry and Graphite Furnace Absorption Spectrometry (44,45). An indirect fluorescent method to quantify the level of

lead in intracellular fluids has been published although there are no commercially available fluorescent probes specific to lead.

Other methods such as Cold Vapor Absorption Spectroscopy, Hydride Generation Absorption Spectroscopy and Flow Injection ICP Optical Emission are specifically for mercury determination due to their high sensitivity and selectivity (45,46).

1.6.1 Inductively Coupled Plasma Mass Spectrometry

In an ICP-MS, a sample is directed through a plasma source where they become ionized and atomized to create small ion fragments that are detected in the mass spectrometer. ICP-MS can detect a low concentration of metals (47).

A heated argon plasma is injected with a fine aerosol of a sample, where it dries the aerosol and atomizes the element. The element is simultaneously ionized and ions are sorted based on the mass-to-charge (m/z) ratio in the mass analyzer (47–49).

The ICP-MS analytical technique is preferred over other methods because of its high sensitivity with detection limits of up to parts per trillion, high throughput and its ability to detect more than one element simultaneously (50,51).

1.6.2 Inductively Coupled Plasma Atomic Emission Spectroscopy

This technique quantifies elements based on exciting the atoms using plasma and analyzing the emission wavelength of the electromagnetic radiation. The electrons release energy at a specific wavelength when they return to the initial state.

1.6.3 Flame Atomic Absorption Spectrometry

The principle is transforming metal ions into their atomic state using a flame (52). The free atoms absorb light in their ground state from a specific wavelength provided by the hollow cathode lamp and measure the amount of light absorbed.

1.6.4 Cold Vapor Atomic Absorption Spectroscopy

This technique uses a high-frequency mercury electrode driven by a low-pressure discharge lamp as an ultraviolet light source that generates extremely narrow bandwidth emission lines that are consistent with the mercury atom absorption lines. This technique is extremely sensitive to the determination of mercury and can measure precision from part per trillion to parts per million (45).

1.6.5 Graphite Furnace Atomic Absorption Spectrometry

A sample is placed in a small graphite tube and heated to atomize the element. The atoms move to higher energy levels as a result of light absorption. In this technique, the atoms absorb light at the characteristic frequencies of the element (52).

1.6.6 Hydride Generation Atomic Absorption Spectroscopy

An element is reduced from the higher oxidation state to its lowest and is converted to the volatile hydride, which is then pumped into the atom cells by an inert gas. It is a flexible technique for determining most metalloids that form hydrides including selenium, arsenic, germanium, antimony, mercury and tin.

1.7 Health risk assessment

1.7.1 Definition

The risk or hazard assessment is the scientific method that assesses the risk to humans of exposure to different types of chemicals such as pharmaceuticals, environmental pollutants, and chemicals in cosmetics (53). Health risk assessment involves the use of a screening tool to identify the associated health risk and monitor health status over time. It involves identifying and estimating the risks posed by these inherent hazards and is measured by incorporating a risk probability measurement and harm severity measure (53).

1.7.2 Goals of health risk assessment

The evaluation aims at assessing health status, estimating health risk levels, informing participants, and providing feedback to encourage behavioral change to reduce health risks. Steps to be taken to assess the health risk involves; identifying hazards and those at risk, hazard characterization, exposure assessment, risk characterization and finally monitoring and reviewing.

1.7.3 Health risk assessment methodology

Risk assessment entails four aspects namely: hazard identification, dose-response evaluation, exposure assessment and risk characterization (54).

Hazard identification is based on toxicological and clinical research where undesirable effects such as irritation, skin sensitization, phototoxicity, mutagenicity, developmental and reproductive toxicity, and carcinogenicity are monitored. This is determined by performing the toxicological tests of the raw materials where the potential hazard could be identified (16,54).

Dose-response assessment determines the relationship between the exposure dose of hazardous compounds and their toxic effect. The dose where No Observed Adverse Effect Level (NOAEL)

was determined using data obtained from repeated dose toxicity studies which in turn was used for the calculation of the Margin of Safety (MOS).

1.7.3.1 Carcinogenic assessment

The carcinogenic risk due to heavy metals was calculated using the Cancer Risk (CR) a method established by the US EPA (4,27,54), which is the likelihood that a person will get cancer due to chemical exposure.

$$CR = CDI \times SF$$

SF stands for the slope factor, whereas CDI stands for the chronic daily intake of metals. SF is given as 1.5, 0.5, 0.0085, 6.3, 1, and 9.8 mg/kg/day for As, Cr, Pb, Cd, Hg and Co respectively (54). When the value of CR is less than 10⁻⁶ then this is negligible while a CR greater than 10⁻⁴ is considered unacceptable (Goetzelet al., 2008).

1.7.3.2 Non-carcinogenic assessment

Hazard Quotient (HQ) and Hazard Index (HI) are used to describing a chemical's risk category (4,6). Hazard Quotient is the ratio of chemical exposure to the level at which there are no expected adverse effects (4). There shall be no potential adverse health effects if the calculated HQ is less than one while HQ of more than one poses a health risk to the population (55). Reference doses for arsenic, chromium, lead, cadmium, mercury and cobalt are given as 0.0003, 0.000015, 0.04, 0.001, 0.0013 and 0.02 mg/kg/day respectively.

Another concept is the Hazard Index (HI), which for substances affecting the same organ is the sum of the HQ used to calculate risk of more than one metal. If the derived HI using target-organ-specific HQ is less than one, then it will not result in adverse effects over a lifetime of exposure (55).

$$HI = \sum HQ = HQ_a + HQ_b + HQ_c + HQ_d + HQ_e + HQ_f$$

Where letters represent individual metals detected in the sample.

According to the US EPA guidelines, heavy metal exposure measurement will be determined from CDI when conducting quantitative health risk assessment (55).

$$CDI = \underline{CS \times SA \times AF \times ABS \times EF \times ED \times CF}$$

$$BW \times AT$$

CS is exposure quantity of the metal in ppm, EF is frequency of exposure in days given as 350 days per year, ED is duration of exposure usually for 30 years, AT is time of exposure in days usually 64.4 and 68.9 years for males and females respectively (56,57). BW is body weight of 70 kg, SA is surface area of 5700 cm², AF is adherence factor, ABS is absorption factor and CF is conversion factor (58).

CHAPTER TWO: LITERATURE REVIEW

2.1 Previous studies on heavy metals in lipsticks and eye shadows

2.1.1 Global reports

Studies conducted on most cosmetic products have revealed a high probability of toxic materials being used during production (55). Research conducted on lipstick available commercially has shown, according to the US FDA (2018), that PCPs contain possible contaminants like metals and hence pose serious health effects(Ayenimo et al., 2009; Oguntibeju et al., 2012).

Although many cosmetics contain levels well above 100 ppm to boost the whitening effect, the US FDA limits the amount of mercury in PCPs to less than 1 ppm (59–61). Acceptable levels should be less than 1 ppm as per WHO recommendations (59).

A study about contact dermatitis caused by creams and other topical applications found that, of the eye shadows tested from different products, 75% contained at least a metal at a concentration greater than 5 ppm (60). Analysis carried out by the Campaign for Safe Cosmetics in the USA found that more than sixty percent of the lipstick sample tested had levels of lead of up to 0.65 ppm (62). The US FDA also analyzed lipsticks and found lead levels of between 0.09 and 3.06 ppm (60).

Heavy metals analysis in commercially available lipsticks in Malaysia showed how effective regulation has aided in significantly reducing the quantities of metals that were available in lipstick. Levels of metals in lipstick brands tested were not associated with any serious carcinogenic or non-carcinogenic health complications. This can be attributed both to the regulatory framework in place in the country as well as the raw materials used for production.

Effective regulation can, therefore, aid other countries to reduce the quantities of metals in cosmetics produced locally (63).

In a study comparing two lipstick products from China and Iran, high levels of metals were reported in Chinese products with lead occurring in 95.9 % of lipsticks at a concentration higher than 20 μ g/g, while Iranian samples had levels lower than 10 μ g/g. In this study, 120 random samples from different countries were analyzed using Flame Atomic Emission Spectroscopy (64–66).

An Iranian study involving fifty samples of lipsticks and eye shadows from different brands randomly picked from cosmetic shops in Isfahan found that lead and cadmium concentrations in lipsticks were $0.08 - 5.2 \,\mu\text{g/g}$ and $4.08 - 60.2 \,\mu\text{g/g}$ respectively, whereas lead levels in eye shadows ranged from 0.85 to $6.9 \,\mu\text{g/g}$ and cadmium 1.54 to $55.59 \,\mu\text{g/g}$ ppm (17).

2.1.2 African reports

Research conducted to determine the metal content in PCPs in the Nigerian market indicated the presence of heavy metals at levels significantly high than the regulatory limits (67). Different samples of Chinese eye shadow products sampled on the Nigerian markets of Zaria, Kano and Kaduna areas analyzed heavy metals using Flame Atomic Absorption Spectroscopy (68) reported differing quantities of metals in all the eye shadows (68).

In another study also carried out in Nigeria to provide information on risks associated with humans, traces of metals were found in lipsticks, eye shadows, lip gloss, eyeliner and other personal care products (5). The metal content was determined using Atomic Absorption Spectroscopy and mean metal concentrations were as follows; cadmium 3.1 - 8. ppm, lead 12 - 240 ppm, chromium 9.1 -

44 ppm, nickel 18 - 288 ppm, copper 1.6 - 80 ppm, cobalt 7.9 - 17 ppm, manganese 12 - 230 ppm, and zinc 18 – 320 ppm (5).

Evaluation of toxic metals in 20 lipsticks sampled from Kumasi, Ghana, lead and cadmium were detected using Flame Atomic Absorption Spectroscopy, with Pb and Cd ranging from 0.2 - 36.70 µg/g and 1.83 - 412.23 µg/g, respectively.

Heavy metals in nail polish, lip glosses, and hair dye in samples obtained from Dar es Salaam were analyzed using Flame Atomic Absorption Spectroscopy where metals were determined after digestion with concentrated acids. The analysis showed that in all the samples tested, lead, zinc, and cadmium were at a concentration ranging from 0.00606 to $37.4 \,\mu\text{g/g}$, 0.022 to $2.6 \,\mu\text{g/g}$ and up to $0.25 \,\text{mg/g}$, respectively (69).

2.1.3 Kenyan data

Studies on the prevalence of heavy metals in PCPs in Kenya have shown there is a high probability of one or more metals being found in different products (70). The study was done in Nairobi, Kenya, to determine the presence of metals in lotions, creams and soaps made of Aloe vera. The heavy metal detected in lotions as mercury, lead, zinc, and manganese in varying quantities. In creams, metals such as mercury, lead, cadmium, zinc, manganese, and chromium were detected in various concentrations. While in soap samples, the detected metals include mercury, lead, cadmium, zinc, manganese, and chromium (36).

Elsewhere, it has been reported that even though labels on cosmetics in the Kenyan market do not indicate the existence of heavy metals, most of them contain significant amounts of metals that may pose serious health risks to consumers. The findings also indicated that the mean quantities

in most products exceeded the minimum levels recommended by the WHO and other regulatory agencies (71).

An investigation comparing the content of metals in the scalp hair between urban and rural dwellers using 240 samples obtained from Nairobi, Mombasa, and Kisumu revealed that the urban population's hair had substantially higher metal content than rural ones. It was noticed that the geographic location among the Kenyan residents had a great influence on the concentration of metal (71).

Additionally, another study reported that face paints contain lead in amounts considered to be detrimental to human health (72,73). The National Quality Control Laboratory and the University of Nairobi collaborated on the investigation where 59 samples of paints were tested and in all the samples lead was detected with the highest concentration being 10.54 ppm (73).

2.2 Health risk assessment for heavy metal in lipstick and eye shadow products

Research conducted in Malaysia evaluating the non-carcinogenic health effect of eye shadows reported Hazard Quotient (HQ) values for chromium less than unity thus indicating no significant health risk to eye shadow users (72).

In a study carried out in Nigeria to provide information on risks associated with humans, traces of metals were found in lipsticks, eye shadows, lip gloss, eye pencils, eyeliner, mascara, and face powders (5,58).

2.3 Problem statement

Personal Care Products (PCPs) are widely used and there is a concern about their toxicity on humans due to the presence of metals. PCPs are weakly regulated in Kenya in terms of quality control and licensing. Deficiency in proper law enforcement and stringent measures leads to unregulated cosmetic products easily entering the market. These products may not be of the right quality and might contain metals as impurities. Heavy metals at levels above the permissible concentrations may lead to human toxicity (13).

There is a higher probability that women consume cosmetic products that may be of questionable quality including having unacceptable levels of metals. This exposes women to relatively higher health risks associated with metals in cosmetics compared to men. Moreover, some metals such as lead may cross the placental barrier of pregnant women and pose danger to the unborn fetus leading to birth defects (74).

Metal such as chromium in cosmetic products is known to cause skin allergies. Additionally, metals are implicated in the etiology of cancer and chronic kidney disease. With the rising prevalence of cancer morbidity and mortality in the country (75), metal analysis and conducting risk assessment would aid in formulating mitigative measures for cancer and kidney disease prevention. This will improve public health in Kenyan society.

2.4 Study justification

Cosmetic use is increasing rapidly in the world. Different chemicals are used in the manufacture, including pigments containing elements that pose a harm to the consumers' health (20). The metals can find their way into the final product as impurities (76). Labeling cosmetics does not indicate the presence of metals as an ingredient or impurity since regulation in the country does not require labeling of the contents in cosmetics but only weight, expiry date, and the name of the manufacturer.

The lack of full enforcement of laws governing the quality of PCPs has led to an increase in the unregulated importation of cosmetic products hence posing risks to consumers. Some individuals manufacture products under unregulated conditions with poor good manufacturing practices without considering hygiene and use untested raw materials that may be contaminated with metals.

2.5 Study Significance

The findings will create awareness among consumers on the health hazardous effects associated with the use of lipsticks and eye shadows containing heavy metals. Also, to the regulatory authority on the importance of full enforcement on regulating and testing all the products entering the market.

It will also help in inspection and postmarket surveillance. Evidence-based policy on the regulation and testing of cosmetics will improve product quality and decrease the disease burden with its impact on the economy.

2.6 Hypothesis

The heavy metal content in lipstick and eye shadow products, marketed in Mombasa County is not within the acceptable limits set by International standards.

2.7 Study objectives

2.7.1 Main objective

The main aim of this study was to test lipstick and eye shadow products marketed in Mombasa County for heavy metals (arsenic, lead, cadmium, chromium, mercury, and cobalt) and to carry out a health risk assessment for metals in the tested lipstick and eye shadow products.

2.7.2 Specific objectives

The specific objectives of this study were:-

- 1. To determine the metal content in lipstick and eye shadow products in Mombasa County.
- To conduct a health risk assessment of metals found in lipsticks and eye shadows in Mombasa County, Kenya.

CHAPTER THREE: METHODOLOGY

3.1 Study design

A cross-sectional approach experimental design was used to determine metal content in lipstick and eye shadow products marketed in Mombasa County.

3.2 Study location

The sample collection site for the research was Mombasa County, situated along the Indian Ocean on Kenya's coastal strip. Mombasa is the second-largest metropolitan city bordered by Kilifi and Kwale Counties. There is a lot of influx of goods in the town via the seaport of Mombasa, through the airport since it is a tourist center, and cross-border via Lungalunga which is Kenya -Tanzania border.

Mombasa was selected because of its cosmopolitan nature and also for the fact that it is a tourist town. The presence of a seaport, airport, and porous borders with neighboring countries allows the influx of several varieties of PCPs that may be difficult to regulate.

Sample analysis was done at Kenya Plant health inspectorate Service (KEPHIS), Nairobi, a government parastatal responsible for ensuring the quality of agricultural inputs and produce. This laboratory was selected because it had an ICP-MS machine, and is accessible to the University of Nairobi.

3.3 Study population

The PCPs of interest were the commonly used lipstick and eye shadow products in Mombasa County. The products included cross-border ones.

3.4 Sampling

Seventy-nine (79) samples of different brands of commonly used lipstick and eye shadow products comprising 58 lipsticks and 21 eye shadows (Appendix 1.1) were obtained from different markets in the four sub-counties to achieve a representative sample. The number selected was based on previous studies done on similar populations (Iwegbue et al., 2016; Omolaoye et al., 2010; Tchounwou et al., 2012).

Samples were obtained from cosmetic shops and open-air markets located in all four sub-counties of Mombasa namely Changamwe, Kisauni, Mvita, and Likoni. The samples include cosmetics which were domestically produced and others which were imported from the United State, Germany, U.A.E, China, India, Iran, and Pakistan.

For confidentiality and blind testing, the products were coded before analysis. The coding was done to conceal information regarding the brand, manufacturer, and country of origin.

3.5 Elemental analysis

3.5.1 Equipment

An Inductively Coupled Plasma-Mass Spectrometry (Agilent® Technologies Manufacturing GmbH & Co. KG, Waldbronn, Germany) as shown in figure 3.1 was used to analyze and quantify the number of metals in lipstick and eye shadow products. The ICP-MS was run with MassHunter 4.3 workstation software version C.01.03 which aided in identifying the chemical elements.



Figure 3. 1: A picture of Agilent® inductively coupled plasma mass spectrometer

Metal-free high-purity water (deionized water) obtained from pure water purification systems comprising both deionizer from ELGA (Veolia Water Solutions & Technologies, United Kingdom) and a double distiller from Aquatron (Bibby Scientific Limited, Stone Staffordshire, United Kingdom) was used throughout the work.



Figure 3. 2: A picture of ELGA water de-ionizer (left) and Aquatron double distiller (right)

3.5.2 Reagents, standards, and solvents

Metal-free high-purity nitric acid (70% v/v), hydrochloric acid (37% v/v), and hydrogen peroxide (100 vol), all from Sigma Aldrich (Bangalore, India) were employed in the sample preparation and digestion. Standards for each metal to be analyzed (As, Cr, Pb, Cd, Hg and Co) were prepared from the certified standard stock solution of high purity.

3.5.3 Equipment calibration

Before analysis, the ICP-MS was calibrated using an aqueous multi-element standard solution of As, Cr, Pb, Cd, Hg and Co all prepared in 5% HNO₃. A multi-element standard of 10 ppm was used as a stock solution. From this serial dilutions were done to obtain other solutions with a concentration of 10, 20, 30, 50, and 100 ppm. A micropipette was used to transfer 0, 100, 200, 300, 500 and 1000 microlitres of the multi-element standard into a well-labeled 100ml volumetric flask. The volumetric flask was then topped up to the mark using 5% nitric acid.

Triplicate determinations were made. The acceptance criteria for calibration were an equivalent mean concentration for each metal and a linearity regression coefficient of not less than 0.99.

3.5.4 Sample preparation

All plastic and glassware were scrubbed, washed, and repeatedly rinsed with distilled water before being immersed overnight for 24 hours in a 5% nitric acid solution. After that, the device was rinsed with deionized water before use.

To remove moisture and maintain constant weight, the solid lipstick and eye shadow samples were dried in an oven at 105°C for two hours. They were then cooled in a desiccator and ground to

powders to improve surface area and reaction susceptibility with the acid mixtures used in the digestion.

Microwave-assisted digested cosmetic samples were digested using nitric acid (70%), hydrochloric acid (37%) and hydrogen peroxide (100 vol.) at high temperature, cooled and then transferred into a volumetric flask, then diluted with deionized water and subjected to ICP-MS analysis. The general sample preparation process followed protocols that have been published (77–79).

3.5.4.1 Procedure for microwave digestion of samples

On a 120 ml polymeric microwave-assisted digestion vessel, 0.2 g of cosmetic sample was slowly mixed with 9 ml of nitric acid (70%) and 1 ml hydrochloric acid, under fume extraction hood. The sample was left to react for approximately 5 min, before the tube was sealed, and digested in a microwave (ETHOS-UP, Milestone s.r.l., Sorisole BG Italy) shown in figure 3.3. Microwave digestion parameters are shown in table 3.1. The sample was heated over 20 min to 150°C and kept at 150°C for another 20 min before cooling kicked in automatically.

After cooling, the tube was unsealed and 3 ml of concentrated hydrogen peroxide added to oxidize the organic matter of residues. The mixture was then heated in a microwave to 150°C over 15 min and retained for 10 min at 150°C. The resulting digest was cooled and filtered through filter paper no. 42 (Merck, 0.45 µm), transferred to a calibrated Pyrex glass beaker (250 ml) and filled to a 250 ml mark with deionized water before ICP-MS analysis. It was then analyzed using ICP-MS and results were recorded using a mass spectrometer. The analysis was done in triplicates.



Figure 3. 3: A photograph of ETHOS UP® high-performance microwave

Table 3. 1: Microwave digestion parameters used in the analysis

Volume in milliliters (ml)							
Matrix	Sample weight (g)	Nitric acid	Hydrochloric acid	Hydrogen peroxide			
Soil	0.5	9	1	3	_		
Sediment	0.5	9	1	3			
Cosmetics	0.2	9	1	3			
Biological tissues	0.3	9	1	3			

Source: SOPs at KEPHIS

3.5.4.2 Preparation of working standards and calibration curves

A multi-element standard as a stock solution equivalent to 10 ppm was used to prepare working standards. Standard solutions containing the target elements (lead, cadmium, arsenic, cobalt, chromium, and mercury) were used to prepare a series of working standards of different concentrations 0, 10, 20, 30, 50 and 100 ppb.

3.6 Quality assurance

To ensure the results' reliability, adequate quality assurance protocols and precautions were followed. Cross-contamination was also avoided by carefully handling the samples in an aseptic technique. Daily quality assurance procedures were conducted and evaluated according to to set internal quality controls for the validity of test results. Solutions consisting of blanks were used to calibrate the ICP-MS on daily basis, then the working standards and samples were analyzed.

3.7 Method verification

This is a process of determing whether the analytical method is appropriate for usage as intended under actual experimental circumstances. This is applied to the method that has already been validated. It is carried out to evaluate the validity of an analytical technique. The method must possess particular qualities, such as selectivity, linearity, range, accuracy, and precision, in order to be suitable for its intended use.

Selectivity refers to how well a method can isolate a certain analyte from other substances in a complex mixture without interference from other components. While precision is the degree to which a set of measurements obtained by multiple sampling agree with one another.

3.7.1 Accuracy

This is the degree to which the analyte's determined value in the sample matches its actual value. To ensure the accuracy of the results the ICP-MS was calibrated using an aqueous multi-element standard solution of As, Cr, Pb, Cd, Hg and Co all prepared in 5% HNO₃ for consistent sensitivity. Calibration standards for metal to be analyzed (As, Cr, Pb, Cd, Hg and Co) were prepared from the standard stock solution of high purity with various series of 0, 10, 20, 30m 50 and 100ppm. Three determinations were done during the calibration of the ICP-MS.

3.7.2 Linearity

When an analytical method can yield test findings that are proportionate to the amount of analyte, this is known as linearity. This helps to get a range which is the difference between the upper and lower limits of concentrations. Calibration curve for each analyzed metal shall be used to plot a graph and give the correlation coefficients and linear equations for the metals.

Instrument calibration was done using a spiked sample that was prepared using a known amount of analyte to the matrix which was identical to the sample of interest. The spiking was done by preparing concentrations of 10 and 30ppm for all the elements and it was done in replicates.

3.8 ICP-MS analytical conditions

The precise assessment of metal content in cosmetic is essential since there is a small window between safe and dangerous levels. Heavy metals can be detected using a variety of methods and the current most commonly employed technique is ICP-MS (80). An ICP-MS (Agilent® Technologies Inc. 2017, G8403A 7900 ICP-MS) was used for element analysis under the

optimized parameters at the power of 2000W with plasma gas at 15 liters per minute, auxiliary gas at 0.2 liters per minute, nebulization of 0.8 L/min and sampling rate at 0.3 ml/min.

3.9 Risk assessment

A risk assessment was carried out for both carcinogenic and non-carcinogenic effects following US EPA guidelines. The HQ was determined to measure the non-carcinogenic hazard of metals while the HI was calculated using target organ-specific HQ. In assessing the cancer risk due to heavy metals, calculations were computed using the target cancer risk (CR).

Both Hazard Quotient (HQ) and Hazard Index (HI) are used to describing a chemical's risk category (6). They are used for measuring the non-carcinogenic risk where the HQ is a ratio of chemical exposure and a level at which there are no expected adverse effects (4,63).

3.10 Data analysis

The results of the type and amount of heavy metal present in the sample were recorded in a sheet comprising information such as the code of the brand analyzed, the metal detected, and its concentration.

Collected data was then recorded in a password-protected excel sheet, counter-checked for any errors, and backed up in google drive to prevent data loss and then transferred into MS Excel to analyze for statistical significance of the descriptive statistics including mean and standard deviation. For Health risk assessment US-EPA guidelines were followed in calculating the CDI, HQ, HI and CR.

3.11 Ethical consideration

Since there were no human subjects involved in the study, permission from the ethics and review committee.was not sought.

CHAPTER FOUR: RESULTS

4.1 Sampling and sample information

Seventy-nine (79) samples of cosmetic products comprising lipstick (58 samples) and eye shadow (21 samples) were collected from the four sub-counties in Mombasa County namely Mvita, Kisauni, Changamwe, and Likoni (Appendix 1.1). Table 4.1 shows the cosmetic samples obtained from various sub-counties of Mombasa County. The sample size was informed by other scientific studies reported in the literature. The number selected was based on previous studies done on similar populations (5,13,68).

Table 4. 1: Cosmetic samples collected from various sub-counties in Mombasa

Subcounty	Samples (n)	Percentage (%)
Changamwe	17	21.5
Mvita	27	34.2
Kisauni	21	26.6
Likoni	14	17.7

4.2 Method verification

The calibration curve for each analyzed metal was plotted (Appendix 1.3) and gave the correlation coefficients and linear equations for the metals as shown in Table 4.2. The correlation coefficient values of the linearity of detector response for the tested metals were all above 0.945 and were considered to be fit for the purpose.

Table 4. 2: Correlation coefficient and equation of the line of best fit of the linearity of the analytical method used

Instrument	Metal	R	\mathbb{R}^2	Equation
ICP-MS	As	0.999	0.999	y = 0.011x - 0.01
	Cr	0.972	0.945	y = 0.071x + 0.40
	Cd	0.999	0.999	y = 0.014x + 0.01
	Hg	0.999	0.997	y = 0.024x - 0.03
	Co	0.999	0.999	y = 0.128x - 0.01
	Pb -206	0.999	0.997	y = 0.097x + 0.15
	Pb -207	0.999	0.998	y = 0.087x + 0.11
	Pb -208	0.999	0.998	y = 0.399x + 0.48

4.3 Accuracy

Instrument calibration was done using a spiked sample that was prepared using a known amount of analyte to the matrix that was identical to the sample of interest. The spiking was done by preparing concentrations of 10 and 30ppm for all the six elements under study (As, Cr, Pb, Cd, Hg and Co) and the procedure of calibration was done in a replicate.

The metal recovered after the spike was as shown below (Table 4.3) and as the result suggests the recovered metals ranged from 71.73% to 102.43% which was within the limit of expected recoveries for spiked samples (60-130%).

Table 4. 3: Percentage recoveries for spiked metals

	Amount (ppb)			
Analyte	Spiked	Recovered	Percentage	Average
Lead	10	9.66	96.60	95.7
	30	28.43	94.76	
Mercury	10	10.89	108.90	102.4
	30	28.79	95.97	
Chromium	5	3.29	65.82	71.7
	15	11.65	77.63	
Arsenic	20	19.61	98.03	97.2
	60	57.85	96.42	
Cobalt	5	4.91	98.14	96.7
	15	14.29	95.24	
Cadmium	20	19.19	95.95	95.6
	60	57.16	95.27	

4.4 Metal content in samples

Arsenic and cobalt were detected at varying concentrations in all the sample brands tested (Table 4.4), while mercury, lead, cadmium and chromium were detected in 71 (89.9%), 63 (79.7%), 15 (19%) and 32 (40.5%) of the samples analyzed respectively (Table 4.5).

Table 4. 4: Metal concentration in the analyzed cosmetic samples in ppm

Code	Subcounty	Туре	As	Cr	Pb	Cd	Hg	Co
LP 01	Mvita	Lipstick	1.084	a	a	a	1.079	0.155
LP 02	Mvita	Lipstick	0.894	a	a	1.207	0.892	0.084
LP 03	Mvita	Lipstick	1.738	13.267	10.583	a	1.862	0.463
LP 04	Mvita	Lipstick	1.008	26.092	0.974	a	0.733	1.307
ES 05	Mvita	E. shadow	1.198	11.763	2.301	a	0.530	1.604
LP 06	Mvita	Lipstick	3.492	0.508	1.019	a	0.913	0.642
LP 07	Mvita	Lipstick	0.544	a	0.213	a	0.469	0.106
LP 08	Mvita	Lipstick	0.661	a	2.433	a	0.386	0.445
LP 09	Mvita	Lipstick	1.241	a	0.280	a	0.372	0.112
LP 10	Mvita	Lipstick	0.723	a	3.528	a	0.464	0.346
LP 11	Mvita	Lipstick	1.062	a	5.882	a	0.772	0.144
LP 12	Mvita	Lipstick	0.456	a	a	a	0.499	1.466
LP 13	Mvita	Lipstick	0.766	a	2.331	a	0.427	0.118
LP 14	Mvita	Lipstick	0.624	173.128	3.595	a	0.321	0.168
ES 15	Mvita	E. shadow	0.956	2.191	6.347	a	0.316	0.856
ES 16	Mvita	E. shadow	1.081	27.349	19.664	a	0.342	1.046
LP 17	Mvita	Lipstick	0.628	a	1.094	a	0.189	0.458
LP 18	Mvita	Lipstick	0.525	a	a	a	0.074	0.147
LP 19	Mvita	Lipstick	1.822	a	2.114	a	0.241	0.208
LP20	Mvita	Lipstick	0.511	a	a	a	0.187	0.382
ES 21	Mvita	E. shadow	1.771	a	18.215	a	0.177	0.626
ES 22	Mvita	E. shadow	3.039	5.886	44.140	a	0.356	1.395
ES 23	Mvita	E. shadow	0.927	a	2.635	a	0.173	0.205
LP 24	Mvita	Lipstick	1.424	a	1.760	a	0.306	1.054
LP 25	Mvita	Lipstick	0.690	a	2.529	a	0.184	0.429
LP 26	Mvita	Lipstick	3.492	14.175	16.878	a	0.073	3.101
LP 27	Mvita	Lipstick	2.813	36.624	6.879	a	0.140	1.605

LP 28	Kisauni	Lipstick	1.037	a	a	a	0.156	0.102
ES 29	Kisauni	E. shadow	1.271	84.121	11.655	a	0.140	0.797
LP 30	Kisauni	Lipstick	0.533	a	a	a	0.090	0.189
LP 31	Kisauni	Lipstick	0.664	5.288	0.332	a	0.248	1.275
LP 32	Kisauni	Lipstick	0.847	a	3.439	a	0.184	0.876
LP 33	Kisauni	Lipstick	0.840	a	2.188	a	0.085	0.500
ES 34	Kisauni	E. shadow	1.154	6.993	2.928	a	0.064	4.228
LP 35	Kisauni	Lipstick	0.821	a	2.899	a	0.017	0.664
LP 36	Kisauni	Lipstick	3.923	46.169	3.272	0.111	0.914	4.778
LP 37	Kisauni	Lipstick	1.176	a	a	a	0.806	1.327
LP 38	Kisauni	Lipstick	0.880	a	3.767	a	0.217	0.388
ES 39	Kisauni	E. shadow	0.796	a	a	0.027	0.160	0.060
LP 40	Kisauni	Lipstick	0.701	a	a	0.059	0.147	0.065
ES 41	Kisauni	E. shadow	0.529	a	a	a	0.267	0.123
LP 42	Kisauni	Lipstick	1.304	a	0.457	a	0.111	3.535
LP 43	Kisauni	Lipstick	0.777	a	0.855	a	0.139	0.348
LP 44	Kisauni	Lipstick	2.465	7.372	3.494	0.140	0.641	0.865
LP 45	Kisauni	Lipstick	1.030	a	a	a	0.479	0.238
ES 46	Kisauni	E. shadow	0.657	a	a	a	0.217	0.004
ES 47	Kisauni	E. shadow	1.574	9.947	17.019	a	0.142	1.531
LP 48	Kisauni	Lipstick	1.084	a	3.089	a	0.064	0.421
LP 49	Changamwe	Lipstick	1.939	0.247	2.421	0.123	0.455	1.927
LP 50	Changamwe	Lipstick	1.852	a	a	a	0.532	0.892
LP 51	Changamwe	Lipstick	0.671	a	0.774	a	a	0.484
LP 52	Changamwe	Lipstick	0.562	a	a	a	0.137	0.319
ES 53	Changamwe	E. shadow	0.690	a	a	a	0.033	0.081
LP 54	Changamwe	Lipstick	3.836	a	1.568	a	a	0.988
ES 55	Changamwe	E. shadow	1.698	1.910	1.709	a	a	1.284
ES 56	Changamwe	E. shadow	0.956	142.880	1.532	a	a	0.260

ES 57	Changamwe	E. shadow	0.759	a	1.426	a	a	0.253
ES 58	Changamwe	E. shadow	0.803	43.868	13.671	1.724	a	0.508
LP 59	Changamwe	Lipstick	0.591	4.620	1.210	0.230	a	0.909
LP 60	Changamwe	Lipstick	0.748	a	0.198	a	a	0.405
LP 61	Changamwe	Lipstick	1.239	4.422	11.628	0.402	1.147	0.234
LP 62	Changamwe	Lipstick	1.899	12.788	11.558	a	0.783	1.184
LP 63	Changamwe	Lipstick	0.815	a	6.273	a	0.386	0.652
LP 64	Changamwe	Lipstick	0.747	a	8.182	a	0.588	0.381
LP 65	Changamwe	Lipstick	0.782	a	13.839	a	0.358	0.550
ES 66	Likoni	E. shadow	0.745	9.116	13.553	a	1.245	0.405
LP 67	Likoni	Lipstick	1.368	a	16.357	a	0.227	0.885
LP 68	Likoni	Lipstick	1.797	1.962	17.524	a	0.354	1.712
ES 69	Likoni	E. shadow	2.332	16.933	7.770	a	1.330	0.363
LP 70	Likoni	Lipstick	0.947	1.763	10.039	a	1.158	0.884
LP 71	Likoni	Lipstick	0.784	17.721	6.066	0.037	0.261	2.164
ES 72	Likoni	E. shadow	1.966	a	2.511	0.009	0.561	1.651
LP 73	Likoni	Lipstick	0.951	a	11.428	0.020	1.551	1.241
LP 74	Likoni	Lipstick	0.845	2.457	2.899	0.047	0.308	0.484
LP 75	Likoni	Lipstick	1.424	3.316	13.405	a	0.428	0.652
LP 76	Likoni	Lipstick	1.105	0.082	11.035	0.041	1.205	1.101
LP 77	Likoni	Lipstick	1.487	a	14.713	a	1.426	0.463
ES 78	Likoni	E. shadow	1.696	a	3.111	a	1.107	0.599
LP 79	Likoni	Lipstick	1.138	16.163	10.053	0.651	1.075	0.607

a= Below detection limits; ppm = parts per million

From the analysis, it was noted that 5 samples representing 6.3% of the total samples analyzed contained arsenic levels greater than the accepted limit of 3 ppm set by the regulatory bodies. The other metals found in greater amounts were chromium at 36.7%, lead at 25.3%, cadmium at 5.1%, mercury at 13.9% and cobalt in 0% of the total samples (Figure 4.1).

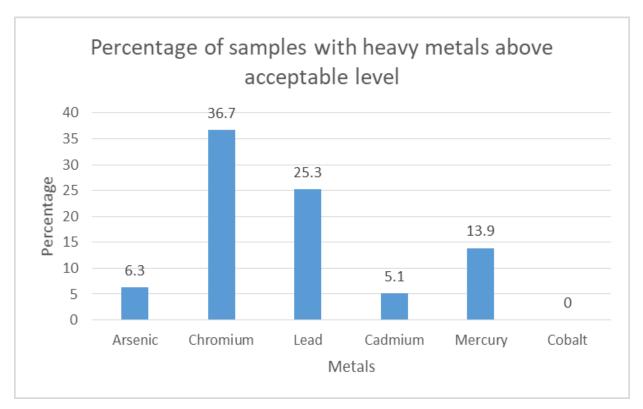


Figure 4. 1: Percentage of samples with heavy metals above the permissible limit

4.5 Concentration of heavy metals in the lipsticks and eye shadows

The results of heavy metal (As, Cr, Pb, Cd, Hg and Co) contamination determined in this study using ICP-MS are presented in table 4.4 (Appendix 1.2). There was great variation in the concentration of metals in PCPs with each sample containing at least more than one heavy metal contaminant. Findings demonstrated that As, Cr, Pb, Cd, Hg and Co were found in 100%, 40.5%, 79.7%, 19%, 89.9% and 100% of total samples respectively (Table 4.5).

The concentrations (mean ± standard deviation) of metals of all the lipsticks (58 samples) analyzed for the heavy metals Cr, Pb, As, Co, Hg and Cd were 6.692±23.986 ppm, 4.432±5.153 ppm, 1.238±0.831 ppm, 0.821±0.874 ppm, 0.47±0.428 ppm and 0.053±0.187 ppm respectively (Table 4.6). The mean concentrations of the metals in the lipsticks in increasing order were Cr (6.7 ppm), Pb (4.4 ppm), As (1.2 ppm), Co (0.8 ppm), Hg (0.5 ppm) and Cd (0.05 ppm).

A similar trend was observed among the eye shadow samples where the mean concentrations of metals were Cr (17.2 ppm), Pb (8.1 ppm), As (1.3 ppm), Co (0.9 ppm), Hg (0.3 ppm) and Cd (0.08 ppm).

Table 4. 5: Percentage of cosmetic samples with heavy metal contamination

Metal	Number of samples (n)	Percentage (%)
Arsenic	79	100.0
Chromium	32	40.5
Lead	63	79.7
Cadmium	15	19.0
Mercury	71	89.9
Cobalt	79	100.0

As seen from the table of results (Table 4.4, 4.6) the content of metals in the lipstick ranges from 0.456 ppm - 3.923 ppm for arsenic, BDL - 173.128 ppm for chromium, BDL - 17.524 ppm for lead, BDL - 1.207 ppm for cadmium, BDL - 1.862 ppm for mercury and 0.065 - 4.778 for cobalt. Among the eye shadows the metal levels were in the range of 0.529 - 3.039 ppm for arsenic, BDL - 142.88 ppm for chromium, BDL - 44.14 ppm for lead, BDL - 1.724 ppm for cadmium, BDL - 1.33 ppm for mercury and 0.004 - 4.228 ppm for cobalt.

Arsenic was detected in all the samples tested with five samples having a concentration higher than the acceptable limits. The mean concentration of arsenic was found to be 1.238±0.831 and 1.267±0.635 ppm for lipstick and eye shadow respectively (Table 4.6). The concentration in some of the lipsticks was very high compared to the limits allowed by regulatory bodies such as WHO and the US FDA which permits a maximum of 3 ppm of arsenic in cosmetic products. So in the brands of PCPs sampled 93.7% of the samples complied with the WHO recommendations having arsenic levels of less than 3 ppm.

The samples with levels higher than the recommended value of arsenic of greater than 3 ppm are four lipsticks and one eye shadow coded as ES 22, LP 06, LP 26, LP 54 and LP 36 with 3.039 ppm, 3.492 ppm, 3.492 ppm, 3.836 ppm and 3.923 ppm respectively (Table 4.4).

Table 4. 6: Mean level of heavy metals in lipsticks and eye shadows

		Maximum		Max						
Type	Metal	limit (ppm)	Min (ppm)	(ppm)	Mean	SD	Median	Mode	Range	RSD
	Arsenic	3	0.46	3.92	1.24	0.83	0.95	1.08	3.46	0.7
	Chromium	1	a	173.13	6.69	23.99	a	a	173.13	3.6
	Lead	10	a	17.52	4.43	5.15	2.43	a	17.52	1.2
	Cadmium	0.3	a	1.21	0.05	0.19	a	a	1.21	3.5
	Mercury	1	a	1.86	0.47	0.43	0.36	a	1.86	0.9
Lipstick	Cobalt	5	0.07	4.78	0.82	0.87	0.49	0.46	4.71	1.1
	Arsenic	3	0.53	3.04	1.27	0.64	1.08	0.96	2.51	0.5
	Chromium	1	a	142.88	17.28	35.06	2.19	a	142.88	2.0
	Lead	10	a	44.14	8.1	10.56	2.93	a	44.14	1.3
	Cadmium	0.3	a	1.72	0.08	0.38	a	a	1.72	4.5
	Mercury	1	a	1.33	0.34	0.41	0.18	a	1.33	1.2
E. shadow	Cobalt	5	0	4.22	0.85	0.95	0.6	N/A	4.22	1.1

a=Below detection limit; ppm = parts per million; N/A = not applicable

From the analysis, it was noted that 5 samples representing 6.3% of the total samples analyzed contained arsenic levels greater than the accepted limit of 3 ppm set by the regulatory bodies. The other metals found in greater amounts were chromium at 36.7%, lead at 25.3%, cadmium at 5.1%, mercury at 13.9% and cobalt at 0% of the total samples (Table 4.7).

Table 4. 7: Percentage of cosmetic samples with metal content higher than acceptable limits

Metal	Percentage (%)	
Arsenic	6.3	
Chromium	36.7	
Lead	25.3	
Cadmium	5.1	
Mercury	13.9	
Cobalt	0	

Chromium was present in the samples tested with 36.7% having a concentration higher than the acceptable limits (Table 4.7). The mean concentration of chromium was found to be 6.692 ± 23.986 and 17.284 ± 35.064 ppm for lipstick and eye shadow respectively (Table 4.6). The concentration in some of the lipstick was very high compared to the limits allowed by a regulatory body such as WHO which permits a maximum of 1 ppm of chromium in cosmetic products. Also according to the European Union, another regulatory body, the permissible limit for chromium is $1\mu g/g$ (1 ppm) This is added as a colorant and according to US EPA, its safe level is 1 ppm(81).

Seventeen lipsticks and twelve eye shadows obtained across the four sub-counties in Mombasa had a concentration of chromium greater than 1 ppm. One sample had much higher levels of chromium (173.128 ppm) with others ranging from 1.763 ppm to 46.169 ppm (Table 4.4). This high level of chromium detected impacted the mean so in this case the median was taken. In

general, 63.3% of the cosmetics had a level of less than 1 ppm which is the acceptable limit by most regulatory bodies.

Lead was found in 79.7% of samples with 25.3% having a concentration higher than the acceptable limits of 10 ppm as per the World Health Organization(82) (Table 4.7). The mean concentration was 4.432±5.153 and 8.104±10.556 ppm for lipstick and eye shadow respectively (Table 4.6). Thirteen lipsticks and seven eye shadow samples had lead levels greater than 10 ppm. One sample tested had an extremely higher amount of lead of up to 44.14 ppm found in the eye shadow ES 22 that was obtained in Mvita Sub County while sixteen samples had undetectable levels that were below detection limits.

Only fifteen samples tested positive for cadmium with only four having levels exceeding the acceptable limit of 0.3 ppm set by WHO (82), the rest had undetectable levels. The samples LP 61, LP 79, LP 02 and ES 58 were found to contain 0.402 ppm, 0.651 ppm, 1.207 ppm and 1.724 ppm respectively. The mean concentration was 0.053±0.189 ppm for lipsticks and 0.084±0.376 ppm for eye shadows.

Of the 89.9% of PCPs containing mercury, eight samples (10.1%) had levels of BDL while eleven comprising (13.9%) had amounts greater than the recommended level of 1 ppm according to WHO (82). The mean concentration of mercury in lipstick was recorded as 0.47±0.428 ppm while that of eye shadows was 0.341±0.406 ppm (Table 4.6), while the levels range from BDL to 1.862 ppm and BDL to 1.33 ppm for the lipstick and eye shadow respectively.

The concentration range of cobalt in the sample tested for the lipstick was 0.065 to 4.778 ppm and 0.004 to 4.224 ppm for the eye shadow. The mean concentration was 0.821±0.874 ppm and 0.851±0.945 ppm for the lipstick and eye shadow samples respectively.

In general, the overall mean concentration of all the PCP sample types (79 samples) collected and analyzed for the six metals As, Cr, Pb, Cd, Hg and Co were 1.25±0.78 ppm, 9.51±27.529 ppm, 5.41±7.116 ppm, 0.06±0.249 ppm, 0.44±0.424 ppm and 0.83±0.887 ppm respectively (Table 4.8).

Table 4. 8: Mean concentrations of heavy metals in the samples of Personal Care Products

Metal	Min (ppm)	Max (ppm)	Mean	Standard Deviation	Median	Mode	Relative Standard Deviation
Arsenic	0.46	3.92	1.25	0.78	0.96	1.08	0.6
Chromium	a	173.13	9.51	27.53	a	a	2.9
Lead	a	44.14	5.41	7.12	2.53	a	1.3
Cadmium	a	1.72	0.06	0.25	a	a	4.1
Mercury	a	1.86	0.44	0.42	0.25	a	1.0
Cobalt	a	4.78	0.83	0.89	0.51	0.46	1.1

a = Below detection limit; ppm = parts per million

Table 4. 9: Comparison of the mean, standard deviation, and Relative Standard Deviation of the heavy metal content in the cosmetic samples

	Concentration (mean ± SD in ppm) (RSD)				
Metals	Lipsticks (n=58)	Eye shadows (n=21)			
As	$1.24 \pm 0.83 (0.67)$	$1.27 \pm 0.64 (0.50)$			
Cr	$6.69 \pm 23.99 (3.58)$	$17.28 \pm 35.06 \ (2.02)$			
Pb	$4.43 \pm 5.15 (1.16)$	$8.10 \pm 10.56 (1.30)$			
Cd	$0.05 \pm 0.19 (3.53)$	$0.08 \pm 0.38 (4.48)$			
Hg	$0.47 \pm 0.43 (0.91)$	$0.34 \pm 0.41 \ (1.19)$			
Co	$0.82 \pm 0.88 (1.06)$	$0.85 \pm 0.95 \ (1.10)$			

4.6 Hypothesis testing

The null hypothesis (H_0) was that the heavy metal content in lipstick and eye shadow products, marketed in Mombasa County is within the acceptable limits set by International standards. While

the alternative hypothesis (H₁) stated that the heavy metal content in lipstick and eye shadow products, marketed in Mombasa County is not within the acceptable limits set by International standards.

The hypothesis was tested using mean at a confidence interval of 95% (CI 95%), and it was noted from the results obtained that the population mean (maximum acceptable limits) was outside the range of lower and upper limits of the 95% confidence interval. This means we reject the null hypothesis and accept the alternative one which states the heavy metal content in lipstick and eye shadow products, marketed in Mombasa is not within the acceptable limits.

Indeed, metal levels in the product sampled were not within the acceptable limits set by International standards. Therefore, the concentrations of metals were much higher than recommended values of 3 ppm, 1 ppm, 10 ppm, 0.3 ppm, 1 and 5 ppm for As, Cr, Pb, Cd, Hg and Co respectively set by the WHO. Tables 4.10 and 4.11 give the lower and higher levels of confidence interval (CI) at 95% CI for each element analyzed.

Table 4. 10: Confidence intervals of lipsticks at 95% CI

			CI (95%)	
Metal	Mean	SD	Lower	Higher
Arsenic	1.24	0.83	1.02	1.45
Chromium	6.69	23.99	0.52	12.86
Lead	4.43	5.15	3.10	5.76
Cadmium	0.05	0.19	0.00	0.10
Mercury	0.47	0.43	0.36	0.58
Cobalt	0.82	0.87	0.60	1.04

Table 4. 11: Confidence intervals of eye shadows at 95% CI

			02 (50 70)	
Metal	Mean	SD	Lower	Higher
Arsenic	1.27	0.63	1.00	1.54
Chromium	17.28	35.06	2.28	32.28
Lead	8.10	10.56	3.58	12.62
Cadmium	0.08	0.38	-0.08	0.24
Mercury	0.34	0.41	0.16	0.52
Cobalt	0.85	0.94	0.45	1.25

It is clear from the calculated CI at 95% confidence intervals for the lipsticks (Table 4.10) of the

CI (95%)

elements As, Pb, Cd and Hg that the accepted limits are outside the CI range meaning we have rejected the null hypothesis and accepted the alternative hypothesis which states that the four heavy metals As, Pb, Cd and Hg in cosmetics are not within the acceptable limits. While the acceptable level for chromium of 1 ppm is within the CI (95%) of (0.52, 12.86), hence we accept the null hypothesis where the chromium content is within the stipulated limits. For the eye shadows, the levels of As, Cr, Cd and Hg are more than the acceptable amount set by the regulatory bodies since the limit is outside the 95% CI (Table 4.11) while lead is within the limits at 95% CI (3.58, 12.62). It is evident that statistical analysis of the study results, on the amount of selected metals found in the lipsticks and eye shadow were significantly different at 95% CI. This may raise alarm, especially for users applying a combination of these products.

4.7: Health risk assessment

Health risks were calculated with values proposed by US EPA to assess health risks posed to human beings. Hazard quotient of six metals in our sampled cosmetics was calculated to determine risk, which is a ratio of metal exposure to chronic reference dose that is given as 0.0003, 0.000015, 0.04, 0.001, 0.0013 and 0.02 mg/kg/day for arsenic, chromium, lead, cadmium, mercury and cobalt respectively (83,84).

The likelihood of the chemicals' harmful consequences is decreased if HQ is lower than one while HQ of greater than one poses risks to the population (85). HI was used to estimate the risk of more than one metal which is the total of HQ for the metals employed (84).

Despite the fact that the carcinogenic risk is the chance that a person would contract cancer as a result of chemical exposure, it is therefore important to quantify the risk to determine the likelihood of developing cancer.

$$HQ = CDI/R_fD$$
 (Refer to section 1.7.3)

$$HI = \sum HQ = HQ_{As} + HQ_{Cr} + HQ_{Pb} + HQ_{Cd} + HQ_{Hg} + HQ_{Co}$$

$$CDI = \underline{CS \times SA \times AF \times ABS \times EF \times ED \times CF}$$

 $BW \times AT$

Carcinogenic risk (CR) =
$$CDI \times SF$$

(Refer to section 1.7.3)

CDI is the daily intake, and SF is slope factor given as 1.5, 0.5, 0.0085, 6.3, 1 and 9.8 mg/kg/day for As, Cr, Pb, Cd, Hg and Co respectively (54). R_fD is the reference dose (Table 4.13). UF is the uncertainty factor and MF is the modifying factor. Tables 4.12 show the parameters for metal exposure.

Table 4. 12: Parameters for metal exposure in cosmetics

Exposure factor	Unit	Value
Exposure concentration (CS)	Ppm	X
Exposure frequency (EF)	days/year	350
Duration of exposure (ED)	year	30
Average time (AT)	days	25550
Bodyweight (BW)	Kg	70
Exposed skin area (SA)	cm ²	5700
Adherence factor (AF)	mg cm ⁻²	0.07
Dermal absorption factor (ABS)		0.001
Conversion factor (CF)	kg/mg	10 ⁻⁶

Note: x = metal mean concentration in a given sample

Table 4. 13: Reference doses in (mg/kg) and cancer slope factor for metals

Cancer slope factor (CSF)

Heavy Metal	$R_{ m f}D$	Oral	Derm al	Inhalatio n
Arsenic	0.0003	1.5	1.5	15
Chromium	0.000015	0.5	-	41
Lead	0.04	0.0085	-	0.042
Cadmium	0.001	6.3	-	6.3
Mercury	0.0013	1	-	1
Cobalt	0.02	9.8	-	9.8

4.7.1: Non-carcinogenicity of metals

The degree of heavy metal toxicity to the biological membrane in human being depends on daily consumption (86). Chronic Daily Intake of the six metals tested in our sample (As, Cr, Pb, Cd, Hg and Co) was determined using the mean concentration of each metal and its effects (Figure 4.2), as well as the metals' maximum tolerable dose intake (MTDI) as shown in table 4.14.

The daily intake of the six metals was found to be 2.92E-09, 2.23E-08, 1.27E-08, 1.43E-10, 1.02E-09, 1.94E-09 mg/day for As, Cr, Pb, Cd, Hg and Co respectively in all samples of PCPs collected which was less than the MTDI of each element.

In the category of lipsticks, the daily intake of the six metals was found to be 2.90E-09 mg/day for As, 1.57E-08 mg/day for Cr, 1.04E-08 mg/day for Pb, 1.24E-10 mg/day for Cd, 1.10E-09 mg/day for Hg and 1.92E-09 mg/day for cobalt whereas in eye shadow category the CDI for the As, Cr, Pb, Cd, Hg and Co was found to be 2.97E-09, 4.05E-08, 1.90E-08, 1.97E-10, 7.99E-10, 1.99E-09 mg/day respectively.

	· 2 3/			
Metals	PCPs	Lipstick	Eye shadow	MTDI
Arsenic	2.92	2.9	2.97	
Chromium	22.3	15.7	40.5	0.2
Lead	12.7	10.4	19	0.21
Cadmium	0.143	0.124	0.197	0.021
Mercury	1.02	1.1	0.799	
Cobalt	1.94	1.92	1.99	

MTDI= maximum tolerable daily intake, CDI= chronic daily intake

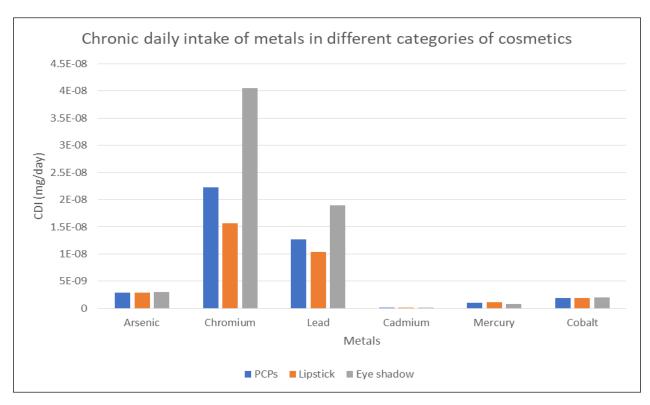


Figure 4. 2: Chronic daily intake of metals

From the results in table 4.15, it is clear that the HQ of the metals obtained under study is less than one, hence users will not experience significant risks through dermal absorption. The calculated HI in this is less than one, hence cosmetics sampled in this study are found to be safe to the users.

Table 4. 15: Non-carcinogenic risks of metals in Personal Care Products

Sample type	HQ _{As}	HQ _{Cr}	HQ_{Pb}	HQ_{Cd}	HQ_{Hg}	HQ_{Co}	HI
PCP	9.73E-06	0.00148	3.17E-07	1.43E-07	7.86E-07	9.71E-08	1.49E-03
Lipstick	9.68E-06	0.00105	2.60E-07	1.24E-07	8.47E-07	9.62E-08	1.06E-03
Eye shadow	9.89E-06	0.0027	4.75E-07	1.97E-07	6.14E-07	9.97E-08	2.71E-03

4.7.2: Carcinogenicity of metals

The risk of developing cancer is evaluated for the carcinogens; where is the product of CDI and SF which is response to carcinogens over an average lifetime. The SF of hazardous substances

understudy is given as 1.5, 0.5, 0.0085, 6.3, 1 and 9.8 mg/kg/day for As, Cr, Pb, Cd, Hg and Co respectively (Table 4.13). The calculated cancer risk is given in table 4.16. The oral exposure pathway is used to calculate the risk assessment because the oral and dermal routes of exposure appear to be equal in risks in all the elements.

The Cancer Risk of the metals in our study was found to be 4.35E-03, 7.85E-03, 8.84E-05, 7.81E-04, 1.1E-03, 1.88E-02 in lipsticks and 4.46E-03, 2.03E-02, 1.62E-04, 1.24E-03, 7.99E-04, 1.95E-02 in eye shadows for As, Cr, Pb, Cd, Hg and Co respectively (Table 4.16).

Interpreting the result when the value of calculated $CR < 10^{-6}$ then is negligible while a CR of greater than 10^{-4} is considered unacceptable (87). Calculated CR of these elements was more than the acceptable of limit 10^{-4} meaning they pose a health risk to consumers. The maximum value of cancer risk was 0.0188 in lipstick and 0.0203 in eye shadows while the minimum was 8.84E-05 and 7.99E-04 in lipstick and eye shadow respectively.

Table 4. 16: Cancer risk index of heavy metals in the cosmetics analyzed

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_	CE	OI of metals (mg	/kg)	Cancer risk index (CRI)				
Metals	PCPs	Lipsticks	Eye shadows	PCPs	Lipstick	Eye shadow		
Arsenic	2.92E-09	2.90E-09	2.97E-09	4.38E-03	4.35E-03	4.46E-03		
Chromium	2.23E-08	1.57E-08	4.05E-08	1.12E-02	7.85E-03	2.03E-02		
Lead	1.27E-08	1.04E-08	1.90E-08	1.08E-04	8.84E-05	1.62E-04		
Cadmium	1.43E-10	1.24E-10	1.97E-10	9.01E-04	7.81E-04	1.24E-03		
Mercury	1.02E-09	1.10E-09	7.99E-10	1.02E-03	1.10E-03	7.99E-04		
Cobalt	1.94E-09	1.92E-09	1.99E-09	1.90E-02	1.88E-02	1.95E-02		

Risk was also assessed by calculating the margin of safety. World health organization proposes a maximum value of MoS of 100, which is acceptable to conclude the safety of the substance (88).

Table 4. 17: Chronic Daily Intake and margin of safety of metals in cosmetics

	As	Cr	Pb	Cd	Hg	Co
Chronic Daily Intake						
Lipstick	2.90E-09	1.57E-08	1.04E-08	1.24E-10	1.10E-09	1.92E-09
Eye Shadow	2.97E-09	4.05E-08	1.90E-08	1.97E-10	7.99E-10	1.99E-09
Margin of Safety						
Lipstick	10344828	95541.401	384615385	806451613	118181818	1.04E+09
Eye Shadow	10101010	37037.037	210526316	507614213	162703379	1.01E+09

The concentration of these metals in some samples was found to be higher than the recommended safe limit for skin protection. The obtained margin of safety was greater than 100, suggesting that the metal concentrations examined in these cosmetics pose no danger associated with their presence. But caution should be taken when using these products as they accumulate in the human body leading to toxicity of biological systems hence causing adverse effects.

CHAPTER FIVE: DISCUSSION

In all the studies done or published, heavy metals were detected in the analyzed samples in varying concentrations. Even though some samples detected heavy metals within acceptable limits, others had concentrations above acceptable levels hence posing health risks to consumers. Comparing this with previously published studies, the trend of metal detection was observed.

The metal concentration in the samples of PCPs is lower than the results attained by other authors, but it is still high enough to be identified and categorized as possibly dangerous. To reduce the risk of sensitization in extremely sensitive individuals, the content of heavy metals in cosmetics, such as Ni and Cr, should be less than 1 ppm (20,89).

The labels of any of the products did not include the metals examined in this investigation as an ingredient. Due to a lack of regulatory control and testing, manufacturers were not even aware of the contamination with these toxic metals (34,90).

Most likely, these pollutants were introduced into the final products due to the use of substandard raw materials or production techniques. Sometimes mercury is added as an ingredient with its role being to lighten the skin (Ricketts et al., 2020). Although some levels, even though within the acceptable range, may imply that the products are safe to be used but caution should be taken in the continual use of these products as minimal absorption keep on accumulating in the body leading to toxic levels.

This study evaluated the amount of six (6) metals As, Cr, Pb, Cd, Hg and Co in 58 samples of lipsticks and 21 samples of eye shadows obtained from the markets of Mombasa County. The mean of these metals in the cosmetic products understudy was reported to be 1.23, 9.51, 5.41, 0.06, 0.4, and 0.83 ppm for As, Cr, Pb, Cd, Hg and Co respectively which were found to be within the

recommended maximum allowable limits set by WHO. However, the mean level of chromium was found to be ten times higher than the recommended limit of 1 ppm. One sample contained a high level of Chromium of about 173ppm and this impacted the mean hence the median value preferred.

The significance of the study is that the findings will create awareness among consumers of the health effects associated with the use of lipsticks and eye shadows containing heavy metals. Also, to the regulatory authority on the importance of full enforcement on regulating and testing all the products entering the market. Evidence-based policy on the regulation and testing of cosmetics will improve product quality and decrease the disease burden.

The results of the current investigation showed that using these cosmetics available in Mombasa markets exposes consumers to metals. The most concerning toxicological substances are lead and mercury because of their high degree of toxicity. Continuous application of these contaminated products leads to the accumulation of metals to toxic levels.

Health and healthcare framework systems in developing countries need to include consumer education regarding the dangers of using substances containing heavy metals. The assessment of dangerous metals in cosmetic products, taking into account their toxicity, has motivated us to conduct this study.

Lead content was found to be higher in 13 samples (22.4%) and 7 samples (33.3%) in lipstick and eye shadow respectively while 16 samples of the PCPs had levels below the detection limit.

Our samples' determined Pb concentrations were below the regulatory thresholds of 10 mg/kg and 20 mg/kg, respectively, established by Canada and the USFDA (91). Additionally, the Pb concentration range in the lotion samples was roughly identical to the amount previously reported by Borowska's study, but it was lower than that reported by Ababneh in body lotions.(16).

Three out of 58 samples (5.2%) of lipstick contained cadmium levels above the maximum acceptable limit of 0.3 ppm while nine samples (15.5%) were found with acceptable levels and 46 samples (79.3%) did not detect the presence of cadmium in the PCPs. Whereas out of 21 samples of eye shadow, one had levels above acceptable limit. The highest value of cadmium in cosmetics ranged from 0.402 to 1.724 ppm. The range of Cd detected in the current study was lower than that reported by Borowska but was nearly equivalent to that previously reported by Ababneh in a 2018 study (16,92).

Fifty-four (54) out of 58 samples (93.1%) of lipstick contained arsenic levels below the maximum acceptable limit of 3 ppm while four samples (6.9%) were found with levels above acceptable limits. Whereas out of 21 samples of eye shadow, 20 were below while one sample had a level above the acceptable limit. The highest value of arsenic in cosmetics ranged from 3.04 to 3.92 ppm.

For chromium content in the lipstick, category 17 samples (29.3%) had levels above recommended 1 ppm while 3 samples (5.2%) had levels below the acceptable limit and 38 samples (65.5%) had levels below the detection limit. While in eye shadows 12 samples (57.1%) had levels above 1 ppm and 9 samples (42.9%) with levels below the detection limit. Comparatively, the chromium level was slightly more in our samples than in a previous report (16).

In the analysis of mercury in the lipstick products, 51 samples (87.9%) had acceptable levels while 3 samples (5.2%) had high levels of 1.862 ppm and only 3 samples with no detection. While in the category of eye shadows 14 samples passed the test with levels within the acceptable range and 4 samples with the content below the detection limit.

CHAPTER SIX: CONCLUSION AND RECOMMENDATIONS

6.1 Conclusion

PCPs marketed in Mombasa county are heavily contaminated with metals. Mean concentrations of the metals in lipsticks were Cr (6.7 ppm), Pb (4.4 ppm), As (1.2 ppm), Co (0.8 ppm), Hg (0.5 ppm) and Cd (0.05 ppm. A similar trend was observed among the eye shadow samples where the mean concentrations of metals were Cr (17.2 ppm), Pb (8.1 ppm), As (1.3 ppm), Co (0.9 ppm), Hg (0.3 ppm) and Cd (0.08 ppm).

The findings do not appear to pose a risk. However, repeated use, inappropriate use, and use for people with some skin lesions, maybe a concern since exposed skin may absorb more of the toxicant metals from lipstick and eye shadows.

The continuous application of cosmetics with metals can increase the absorption in the biological system. Since effects of heavy metals can be detrimental to human health, it is necessary to make an effort to inform general public about the risks.

The majority of the lipsticks and eye shadows in the Mombasa markets are from Asia comprising about 76% of the collected samples with China contributing 43% and Dubai 14%.

6.2 Recommendations

6.2.1 Recommendations to the regulatory bodies

The regulatory bodies and the government should put measures and policies in place and regulate its manufacture, importation, and entry into the market by testing all the products before allowed into the shelves for customers' use.

Cosmetics should be analyzed for the presence of heavy metals before authorization into the market to ensure safety. Postmarketing surveillance is also recommended where sampling should be done after a given period to ascertain the quality and safety of cosmetic products. High priority to be given to heavy metal that is of public health concern such as mercury and lead due to their high degree of toxicity.

6.2.2 Recommendation to policymakers

Manufacturers should test their final products and label them appropriately including the presence of metals if any so that users may be aware. Also, regulatory bodies should implement policies where manufacturers are compelled to state on the labels all the contents of the cosmetic products. Stringent fines and revocation of licenses should be introduced for anyone breaking the law regarding the importation of safe cosmetics.

6.2.3 Recommendation for further studies

More research is needed to create a link between exposure to these metals found in PCPs and the diseases they cause. The results could help in the development of policy interventions that will protect consumers from the health hazards associated with metals.

Given that the emphasis of this research was on evaluating the health risks posed by heavy metals by oral and dermal contact, other exposure mechanisms such as inhalation of air or dust should be considered when conducting a complete human health risk assessment.

6.3 Study limitations

Due to budgetary constraints, only the six metallic elements (As, Cr, Pb, Cd, Hg, Co) were determined yet the products could be having other metals. Also, the cosmetic products characterized were not classified according to formulation type.

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APPENDICES

Appendix 1. 1: Samples collected

LIPST	ICK			
S/No	Code	Cosmetic type	Country	Exp date
1	LP 01	Lipstick	China	Oct-24
2	LP 02	Lipstick	China	Nov-22
3	LP 03	Lipstick	China	Jun-22
4	LP 04	Lipstick	Pakistan	Jun-22
5	LP 06	Lipstick	India	Dec-21
6	LP 07	Lipstick	China	Sep-21
7	LP 08	Lipstick	Malaysia	Nov-22
8	LP 09	Lipstick	China	Jun-23
9	LP 10	Lipstick	China	Dec-20
10	LP 11	Lipstick	Korea	Mar-22
11	LP 12	Lipstick	Philippines	Jan-23
12	LP 13	Lipstick	USA	Sep-22
13	LP 14	Lipstick	China	Mar-23
14	LP 17	Lipstick	China	Apr-21
15	LP 18	Lipstick	Dubai	Oct-24
16	LP 19	Lipstick	USA	Nov-22
17	LP20	Lipstick	China	Jun-22
18	LP 24	Lipstick	China	Jun-22
19	LP 25	Lipstick	USA	Dec-21
20	LP 26	Lipstick	France	Oct-24
21	LP 27	Lipstick	USA	Nov-22
22	LP 28	Lipstick	India	Jun-22
23	LP 30	Lipstick	India	Jun-22

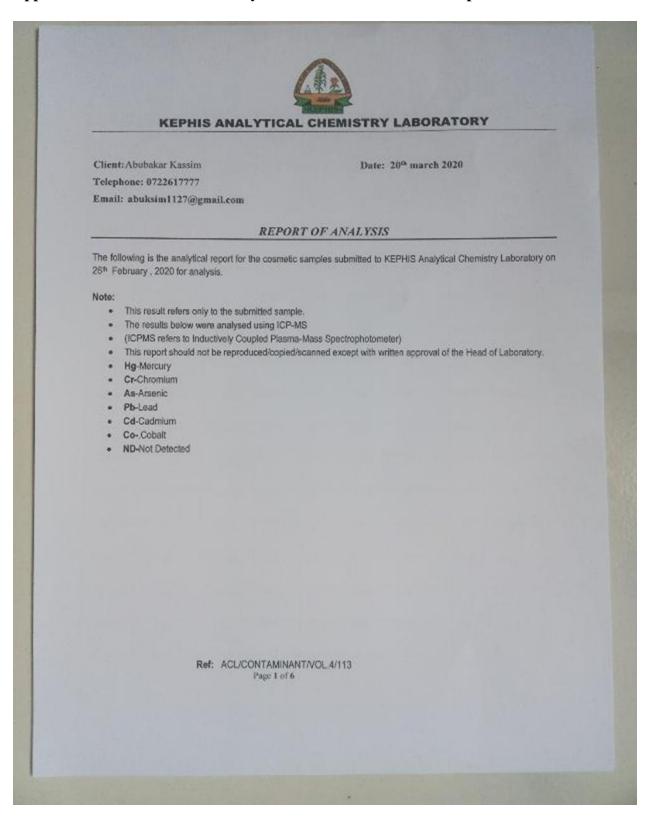
24	LP 31	Lipstick	China	Dec-21
25	LP 32	Lipstick	USA	Sep-21
26	LP 33	Lipstick	Dubai	Nov-22
27	LP 35	Lipstick	China	Jun-23
28	LP 36	Lipstick	China	Dec-20
29	LP 37	Lipstick	France	Mar-22
30	LP 38	Lipstick	Dubai	Jan-23
31	LP 40	Lipstick	UK	Sep-22
32	LP 42	Lipstick	Bordeaux	Jun-21
33	LP 43	Lipstick	Dubai	Oct-24
34	LP 44	Lipstick	China	Nov-22
35	LP 45	Lipstick	India	Jun-22
36	LP 48	Lipstick	China	Jun-22
37	LP 49	Lipstick	China	Dec-21
38	LP 50	Lipstick	India	Dec-20
39	LP 51	Lipstick	China	Feb-24
40	LP 52	Lipstick	China	Dec-21
41	LP 54	Lipstick	Pakistan	Nov-20
42	LP 59	Lipstick	Italy	Oct-24
43	LP 60	Lipstick	USA	Nov-22
44	LP 61	Lipstick	China	Jun-22
45	LP 62	Lipstick	Dubai	Jun-22
46	LP 63	Lipstick	Pakistan	Dec-21
47	LP 64	Lipstick	Canada	Sep-21
48	LP 65	Lipstick	Pakistan	Nov-22
49	LP 67	Lipstick	China	Jun-23
50	LP 68	Lipstick	Dubai	Dec-20
51	LP 70	Lipstick	Iran	Mar-22
52	LP71	Lipstick	Canada	Jan-23

53	LP 73	Lipstick	Turkey	Sep-22
54	LP 74	Lipstick	China	Sep-21
55	LP 75	Lipstick	China	Nov-22
56	LP 76	Lipstick	Canada	Jun-23
57	LP 77	Lipstick	China	Dec-20
58	LP 79	Lipstick	Philippines	Mar-22

EYE SH	HADOW			
S/No	Code	Cosmetic type	Country	Exp date
1	ES 05	Eye shadow	China	Oct-24
2	ES 15	Eye shadow	USA	Nov-22
3	ES 16	Eye shadow	China	Jun-22
4	ES 21	Eye shadow	Dubai	Jun-22
5	ES 22	Eye shadow	Dubai	Dec-21
6	ES 23	Eye shadow	Dubai	Dec-20
7	ES 29	Eye shadow	China	Mar-22
8	ES 34	Eye shadow	China	Mar-24
9	ES 39	Eye shadow	China	Apr-22
10	ES 41	Eye shadow	Sweden	Oct-24
11	ES 46	Eye shadow	USA	Nov-22
12	ES 47	Eye shadow	England	Jun-22
13	ES 53	Eye shadow	India	Jun-22
14	ES 55	Eye shadow	Dubai	Dec-21
15	ES 56	Eye shadow	China	Sep-21
16	ES 57	Eye shadow	Dubai	Nov-22
17	ES 58	Eye shadow	China	Jun-23
18	ES 66	Eye shadow	China	Dec-20
19	ES 69	Eye shadow	China	Mar-22
20	ES 72	Eye shadow	China	Jan-23
21	ES 78	Eye shadow	China	Sep-22

^{*}Sample collection period: January and February 2020

Appendix 1. 2: Raw results of heavy metal content in cosmetic samples



Lab code	Client	Sample	As	Cr	Pb	Cd	Hg	Co
	identification codes	Туре	(mg/Kg)	(mg/Kg)	(mg/Kg)	(mg/Kg)	(mg/Kg)	(mg/Kg)
CA200330	1	Lipstick	1.084	ND	ND	ND	1,079	0.155
CA200331	2	Lipstick	0.894	ND	ND	ND	0.892	0.084
CA200332	3	Lipstick	1.738	13.267	10.583	1.207	1.862	0.463
CA200333	4	Lipstick	1.008	26.092	0.974	ND	0.733	1.307
CA200334	5	Eye shadow	1.198	11.763	2.301	ND	0.530	1.604
CA200335	6	Lipstick	3.492	0.508	1.019	ND	0.913	0.642
CA200336	7.	Lipstick	0.544	ND	0.213	ND	0.469	0.106
CA200337	8	Lip gloss	0.661	ND	2.433	ND	0.386	0.445
CA200338	9	Lipstick	1.241	ND	0.280	ND	0.372	0.112
CA200339	10	lip gloss	0.723	ND	3.528	ND	0.464	0.346
CA200340	11	Lipstick	1.062	ND	5.882	ND	0.772	0.144
CA200341	12	Lip gloss	0.456	ND	ND	ND	0.499	1.466
A200342	13	Lipstick	0.766	ND	2.331	ND	0.427	0.118
A200343	14	Lip gloss	0.624	173.128	3.595	ND	0.321	0.168
A200344	15	Eye shadow	0.956	2.191	6.347	ND	0.316	0.856

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CA200345	16	Eye shadow	1.081	27,349	19.664	ND	0.342	1,046
CA200346	17	Up gloss	0.628	NO	1.094	ND	0.189	0.458
CA200347	18	Lipstick	0.525	ND	ND	NO.	0.074	0.147
CA200348	19	Lipstick	1.822	ND	2.114	ND	0.241	0.208
CA200349	20	Lipstick	0.511	ND	ND	ND	0.187	0.382
CA200350	21	Eye shadow	1.771	ND	18.215	ND	0.177	0.626
CA200351	22	Eye shadow	3.039	5.886	44.140	ND	0.356	1.395
CA200352	23	Eye shadow	0.927	ND	2.635	NO	0.173	0.205
CA200353	24	Lip gloss	1,424	ND	1.760	ND	0.306	1.054
CA200354	25	Lipstick	0.690	ND	2.529	ND	0,184	0.429
CA200355	26	Lipstick	3.492	14.175	16.878	ND	0.073	3.101
CA200356	27	Lipstick	2.813	36.624	6.879	ND	0.140	1.605
CA200357	28	Lipstick	1.037	ND	ND	ND	0.156	0.102
CA200358	29	Eye shadow	1.271	84.121	11.655	ND	0.140	0.797
CA200359	30	Lip glass	0.533	ND	ND	ND	0.090	0.189
CA200360	31	Lipstick	0.684	5.288	0.3323	NO	0.248	1.275
CA200361	32	Lip gloss	0.847	ND	3.4387	NO NO	0.184	0.876
CA200362	33	Lipstick	0.840	ND	2.1884	ND	0.085	0.500

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CA200363	34	Eye shadow	1,154	6.993	2.9276	ND	0.064	4.228
CA200364	35	Lip gloss	0.821	ND	2.8990	ND	0.017	0.664
CA200365	36	Lipstick	3.923	46.169	3.2717	0.111	0.914	4.778
CA200366	37	Lip gloss	1.176	ND	ND	ND	0.806	1.327
CA200367	38	Lip gloss	0.880	ND	3.767	ND	0.217	0.388
CA200368	39	Eye shadow	0.796	ND	ND	0.027	0.160	0,060
CA200369	40	Lipstick	0.701	ND	ND	0.059	0.147	0.065
CA200370	41	Eye shadow	0.529	ND	ND	ND	0.267	0.123
CA200371	42	Lipstick	1.304	ND	0.457	ND	0.111	3.535
CA200372	43	Lip gloss	0.777	ND	0.855	ND	0.139	0.348
CA200373	44	Lipstick	2.465	7.372	3,494	0.140	0.641	0.865
CA200374	45	Lipstick	1.030	NO	ND	ND.	0.479	0.238
CA200375	46	Eye shadow	0.657	ND	ND	ND	0.217	0.004
CA200376	47	Eye shadow	1.574	9.947	17.019	ND	0,142	1.531
CA200377	48	Lipstick	1.084	ND	3.089	ND	0.064	0.421
CA200378	50	Lip gloss	1.852	ND	NO	ND	0.532	0.892
CA200379	51	Lip gloss	0.671	ND.	0.774	NO	ND	0.484
A200380	52	Lip gloss	0.562	ND	ND	NO	0.137	0.319

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CA200381	53	Eye pencil	0.690	ND	ND	NO	0.033	0.081
CA200382	54	Lip gloss	3.836	ND	1.568	ND	ND	0.968
CA200383	55	Eye shadow	1.698	1.910	1.709	ND	NO	1.284
CA200384	56	Eye shadow	0.956	142.880	1.532	ND	NO.	0.260
CA200385	57	Eye shadow	0.759	ND	1.426	ND	ND	0.253
CA200386	58	Eye shadow	0.803	43.858	13.671	1.724	ND	0.508
CA200387	59	Lipstick	0.591	4.620	1.210	0.230	ND	0.909
CA200388	60	Lipstick	0.748	ND	0.198	ND	ND	0.405
CA200389	49	Lipstick	1.939	0.2473	2,421	0.123	0.455	1.927

Analyst:

Confirmed by:

Paul Njuguna

Lucy Namu

Lab-technologist

Laboratory Manager

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QUALITY CONTROL

SPIKES

Lead 10ppb spike-9.66ppb = 96.6% recovery

30ppbspike=28.427ppb=94.7% recovery

Mercury 10 ppb spike=10.890ppb=108.90% recovery

30ppb spike=28.790ppb=95.25%recovery

Chromium 5ppb spike-3,291ppb=65.82%recovery

15ppb spike=11.645ppb=77.63%recovery

Arsenic 20ppb spike=19.606ppb=98.03%recovery

60ppb spike=57.854ppb=96.42%recovery

Cobalt 5ppb spike=4.907pph=98.14%recovery

15ppb spike=14.286ppb=95.25%recovery

Cadmium 20ppb spike=19.190ppb=95.95%recovery

60ppb spike-57.160ppb=95.26%recovery

Expected recoveries range for spiked samples should be between 60%-130%

Note

A spiked sample is a sample prepared by adding a known quantity of analyte to a matrix which is close to or identical to that of the sample of interest. Spiked samples may be used in method validation experiments to help identify matrix effects and determine the recovery of an analyte or the selectivity of the method.

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KEPHIS ANALYTICAL CHEMISTRY LABORATORY

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REPORT OF ANALYSIS

The following is the analytical report for the Cosmetics samples submitted to KEPHIS Analytical Chemistry Laboratory on, 26th February, 2020 for analysis.

Note:

- . This result refers only to the submitted sample.
- The results below were analysed using ICP-MS
- (ICPMS)refers to Inductively Coupled Plasma-Mass Spectrophotometer
- This report should not be reproduced/copied/scanned except with written approval of the Head of Laboratory.
- BDL =below detection limits.
- Hg-Mercury

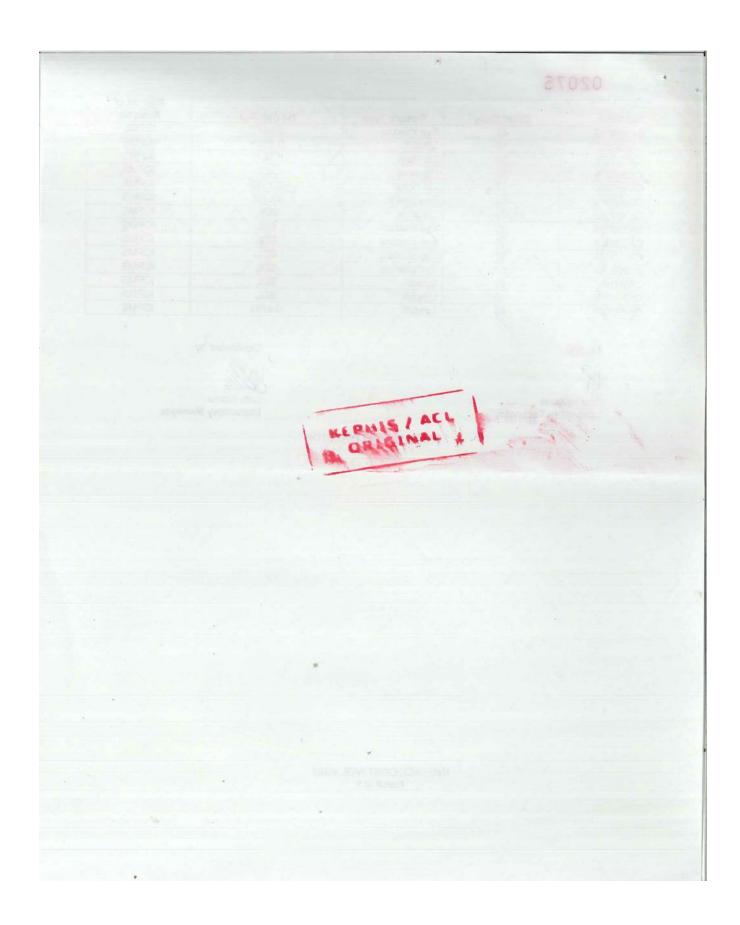
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02036

Lab Code	Client Code	Sample Type	Hg (mg/Kg)	Method of Analysis
CA200330	1	Lipstick	1.0795	ICPMS
CA200331	2	Lipstick	0.8916	ICPMS
CA200332	3	Lipstick	1.8621	ICPMS
CA200333	4	Lipstick	0.7334	ICPMS
CA200334	5	Eye shadow	0.5299	ICPMS
CA200335	6	Lipstick	0.9125	ICPMS
CA200336	7	Lipstick	0.4690	ICPMS
CA200337	8	Lip gloss	0.3856	ICPMS
CA200338	9	Lipstick	0.3717	ICPMS
CA200339	10	lip gloss	0.4638	ICPMS
CA200340	11	Lipstick	0.7716	ICPMS
CA200341	12	Lip gloss	0.4986	ICPMS
CA200342	13	Lipstick	0.4273	ICPMS
CA200343	14	Lip gloss	0.3212	ICPMS
CA200344	15	Eye shadow	0.3160	ICPMS
CA200345	16	Eye shadow	0.3421	ICPMS
CA200346	17	Lip gloss	0.1891	ICPMS
CA200347	18	Lipstick	0.0743	ICPMS
CA200348	19	Lipstick	0.2412	ICPMS
CA200349	20	Lipstick	0.1873	ICPMS
CA200350	21	Eye shadow	0.1769	ICPMS
CA200351	22	Eye shadow	.0.3560	ICPMS
CA200352	23	Eye shadow	0.1734	ICPMS
CA200353	24	Lip gloss	0.3056	ICPMS
CA200354	25	Lipstick	0.1839	ICPMS
CA200355	26	Lipstick	0.0726	ICPMS
CA200356	27	Lipstick	0.1404	ICPMS
CA200357	28	Lipstick	0.1560	ICPMS
CA200358	29	Eye shadow	0.1404	ICPMS
CA200359	30	Lip gloss	0.0900	ICPMS
CA200360	31	Lipstick	0.2482	ICPMS
CA200361	32	Lip gloss	0.1839	ICPMS
CA200362	33	Lipstick	0.0847	ICPMS
CA200363	34	Eye shadow	0.0639	ICPMS
CA200364	35	Lip gloss	0.0169	ICPMS
CA200365	36	Lipstick	0.9142	ICPMS
CA200366	37	Lip gloss	0.8064	ICPMS
CA200367	38	Lip gloss	0.2169	ICPMS
CA200368	39	Eye shadow	0.1595	ICPMS
CA200369	40	Lipstick	0.1473	ICPMS
CA200370	41	Eye shadow	0.2673	ICPMS
CA200371	42	Lipstick	0.1108	ICPMS
CA200372	43	Lip gloss	0.1386	ICPMS
CA200373	44	Lipstick	0.6412	ICPMS
CA200374	45	Lipstick	0.4795	ICPMS
CA200375	46	Eye shadow	0.2169	ICPMS

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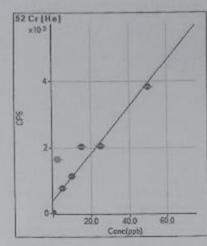
1 - 1 - 0 - 1 -		ST THE STATE OF TH		Method of
Lab Code	Client Code	Sample Type	Hg (mg/Kg)	Analysis
CA200376	47	Eye shadow	0.1421	ICPMS
CA200377	48	Lipstick	0.0639	ICPMS
CA200378	50	Lip gloss	0.5317	ICPMS
CA200379	51	Lip gloss	BDL	ICPMS
CA200380	52	Lip gloss	0.1369	ICPMS
CA200381	53	Eye pencil	0.0326	ICPMS
CA200382	54	Lip gloss	BDL	ICPMS
CA200383	55	Eye shadow	BDL	ICPMS
CA200384	56	Eye shadow	BDL	ICPMS
CA200385	57	Eye shadow	BDL	ICPMS
CA200386	58	Eye shadow	BDL	ICPMS
CA200387	59	Lipstick	BDL	ICPMS
CA200388	60	Lipstick	BDL	ICPMS
Ca200389	49	Lipstick	0.4551	ICPMS
Luborate	ory Technologist	77	Laboratory N	lallayel
		FOR: MANAGING DIRECT		TOTALE OF
	THE STATE OF THE S			TOTAL PARTY OF THE



Appendix 1. 3: Calibration curves

			TRALES	
Desc)	h Polder:	D VAgilime (CPMON) (DATA) 11 (01 2020 CC	SMETICS_CA200330-3853A	
Analy	ysis File:	11_03_2020_COSMETICS_CA200330-389.bit	etchibie	
	Date-Time	3/13/2020 4:34:45 PM		
	oration Title pration Method:			
	Piterpolation Fit:	External Calibration		
Litte		Standard Data File	Sample Name	Aca, Date Time
	1 009CAURA		Back	3/31/2020 2:33:02 PM
-	Z 004CALSd		STD 2 5899	M/11/2020 23437 PM
	3 005CALS.d		STD 3-20 PPB	3/33/2020 2.55.36 PM.
	4 COSCALS d		\$10 4.20 PFB	3/11/2020 2 36:55 996
	5 007CALS.d		STD 5 30 PPB	3/\$1/0000 23837.PM
-	8 DOBCALS d		STD 6 50 PPR	3/31/2020 2:39:37 PM
	7 009CALS.d		STD 7 100 FFB	3/31/0020 2:4037 PM
		Page 1		
		Figs.1		
		Page 1		

Calibration for 007CALS.d



	Rict	Conc.	Cale Conc	CPS	Ratio	Det.	RSD
1	183	0.00	-5.30	2570.30	315	P	
2	123	2.50		164342.06		P	0,6
3		5.00	5.34	78081,78		P	0.2
4	B	10.00	10.43	114216.31		P	0.9
5	0	15.00	22.83	202291.87		P	12
8	E	25.00	23.33	205828.64		P	1,4
7	0	50.00	48.36	383533.51		P	0.3

y = 7099.358397 *x + 40181.628609

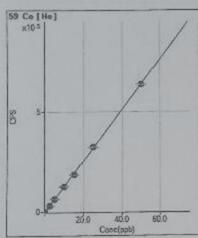
R = 0.9721

DL = 0

8EC = 5.66

Weight: <None>

Min Conc. 0



	Rjet	Conc.	Calc Conc.	CPS	Ratio	Det	RSD
1		0.00	0.14	1120.08		P	
2		2.50	2.53	31694.08		P	0,7
3		5.00	5.05	63902.64		ρ	0.5
4	四	10.00	9.92	128241,83		P	1.6
5	10	15.00	14.53	185113.02		P	2.2
6	1	25.00	25.35	323520.74		P	1.8
7		50.00	49,97	638399.65		P	0.8

y = 12788.050456 * x - 674.769145

R = 0.9999

DL = 0

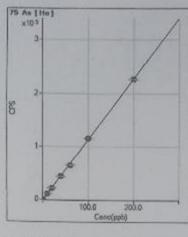
8EC = -0.05277

Weight <None>

Min Conc 0

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Calibration for 007CALS.d



	Rjet	Conc	Calc Cons.	CPS	Retio	Det	RSD
1	問	0.00	0.67	10.00		p	
2	ES	10.00	10.39	11071.54	1	p	1.0
3	四	20.00	19.95	21968.31		P	2.5
4	10	40.00	39.37	44058.71		p	0.9
5	13	60.00	57.98	65246.31		P	0.9
6	8	100.00	101.80	115125.53		p	0.5
7	=	200.00	199.81	220093.75		p	0.5

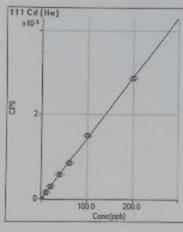
y = 1138.315597 * x - 757.364763 R = 0.9999

DL = 0

BEC = -0.6653

Weight: <None>

Min Conc: 0



	Rict	Canc.	Calc Conc.	CPS	Ratio	Det	RSD
1		0.00	-0.22	40.00		p	
2	23	10.00	9.85	14528.41		p	2.7
3	10	20.00	20.08	29239.76		P	2.9
4		40.00	39.49	57160.17		P	1.7
5	13	60.00	58.34	84259.48		P	0.8
8		100.00	103.72	149532.76		p	0.5
7	四	200.00	198.74	286174.27		P	0.3

y = 1438.142990 * x + 361.908685 R = 0.9997

DL = 0

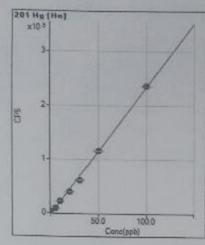
BEC = 0.2517

Weight: <None> Min Conc 0

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Calibration for 007CALS.d



	Rict	Conc.	Calc Conc	CPS	Ratio	Oat.	RSD
1	10	0.00	2.50	3170.54		P	
2	10	5.00	4.90	8589.94		P	1.3
3	8	10.00	10.81	22560.69		P	2.3
4	B	20.00	18,09	39733.49		p	1.4
5		30.00	27.38	81675,16		P	1.7
6		50.00	50.27	115710.31		P	0.5
7	E	100.00	100.96	235404,54		P	1.1

y = 2361.064425 * x - 2969.169255

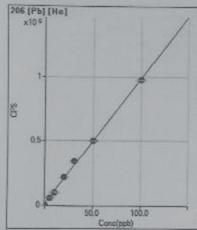
R = 0.9987

DL = 0

BEC = -1.258

Weight: <None>

Min Conc. 0



	Rict	Conz	Calc Conc.	CPS	Ratio D	et RSD
1	0	0.00	-1.48	520.03	1	
2	10	5.00	4.35	57167.49	1	1.2
3	B	10.00	8.83	100588.48	-	0.5
4	B	20.00	20.73	216225.34	F	0.9
5	0	30.00	33.71	342289.70	-	0.5
6		50.00	49.94	499927.34	F	1.0
7		100.00	98.92	975518.37	F	0.2

y = 9710.955431 * x + 14925.904146

R = 0.9987

DL = 0

BEC = 1.537

Weight <None>

Min Conc: 0

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