Investigation and Health Risk Assessment of Potentially Toxic Elements (PTEs) in Selected Hair Dye Products

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Certification

This is to certify that **Sakirat Dasola DANJUMA** with matriculation number **LCU/PG/001323** carried out this research work titled "Investigation and Health Risk Assessment of Potentially Toxic Elements (PTEs) in Selected Hair Dye Products" in the Department of Chemical Sciences, Faculty of Natural and Applied Sciences, Lead City University, Ibadan, Oyo State, for the award of Master of Science Degree (MSc) in Analytical Chemistry and that this has not been previously submitted.

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Dedication

The entire thesis is a tribute to Almighty Allah and my dear parents Mr. and Mrs. Ganiyu, for their unwavering love and support throughout my life.

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I humbly acknowledge the Management of Lead City University and Chemical Science Department.

My thanks go to my mentor and able supervisor Dr. O.O. John-Dewole for his patience, encouragement, monitoring, proof-reading and tutoring. I appreciate my HoD, Prof. O.M. Ighodaro and also to all my Lecturers and the Laboratory Technologists in the Department of Chemical Science, Lead City University for their guidance and tutelage.

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Even though the above-mentioned institutions and persons have assisted in the process of this research work, I alone stand responsible for the errors, if any, found in this work.

Abstract

Hair dye products have recently been implicated as another human exposure route to PTEs. This study investigated the presence and levels of PTEs in five different brands of hair dye products (labelled; A1(Black), A2(Green), A3(Gold), A4(White), and A5(Wine)respectively) using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and the attending health risks. The concentrations of 22 PTEs; Silver, Arsenic, Boron, Cerium, Cadmium, Cobalt, Chromium, Cesium, Copper, Iron, Mercury, Magnesium, Manganese, Molybdenum, Nickel, Palladium, Lead, Sulphur, Antimony, Selenium, Silicon and Zinc were determined. The studied PTEs concentrations were ranged; Cs > Mg > Si > Fe > Pd > Pb > Ag > Zn > Mn > Se > Ni > Ce > Sb > As > Cr > B > Cu > Mo > Co > Cd > S > Hg respectively. The average PTEs concentration ranged as (1074.149 > 882.715 > 720.246 > 689.242 >7.845) ppm for A4 >A1 >A5 > A2 and A3 respectively. The values for Ag, Ce, Cs, Fe, Mg, Mn, and Si were all above the United State Food and Drugs Administration (USFDA) limits, while those of As, B, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pd, Pb, S, and Zn were below the limits in all the samples except for Se in A2, and A3 with the values of 1.21 and 1.18 respectively. Lifetime cancer risk (LCR) values of PTEs through inhalation were in decreasing order of Cr > Co > As > Ni > Cd > Pb and were all above the limits except for Ni in A5. The values of LCR dermal analyzed for adults were found in the order of A5 > A4 > A1 > A2 > A3. In Conclusion, frequent use of these hair dyes products may pose cancer risks and elemental toxicity through dermal contact, ingestion and inhalation.

Keywords: Dermal Exposure, Heavy metals, Hazard Index, ICP-OES, Life-time Cancer Risk

Word Count: 296

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List of Acronyms

Abbreviations	Meaning
AAS	Atomic Absorption Spectrometry
CMC	Cell Membrane Complex
DERM	Dermal
F AAS	Flame Atomic Absorption Spectrometry
GF AAS	Graphite Furnace Atomic Absorption Spectrometry
HCPs	Human Care Products
HDPs	Hair Dye Products
HI	Hazard Index
HQ	Hazard Quotient
IARC	International Agency for Research on Cancer
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ING	Ingestion
INH	Inhalation
PTEs	Potential Toxic Elements
ROS	Reactive Oxygen Species
USEPA	United States Environment Protection Agency
USFDA	United States Food Drug and Administration
WHO	World Health Organization

Chapter One

Introduction

1.1 Background to the Study

Hair is a complicated structure made up of numerous parts that work together to protect the scalp biologically and to provide physical attractiveness to one's self-perception of beauty. In today's world, hair care and styling are crucial aspects of life for both men and women. As a result, dermatologists' medical practice now places greater emphasis on understanding hair products, their mechanisms of action, their efficacy, their ingredients, and hair procedures[1]. PTEs, or potentially harmful components, pose the greatest risk to human health. These metals have been the subject of in-depth investigation, and international organizations like the World Health Organization (WHO) periodically assess their impact on human health. Even though there are a number of long-established negative health impacts of heavy metals, PTE exposure persists. If ingested over an extended period of time, toxic substances can be exceedingly hazardous even at low concentrations[2].

Because PTEs are so prevalent in our surroundings, it is challenging to escape their influence on human health. The human body requires some PTEs, but only in trace amounts[3]. PTEs are known to be found in a variety of cosmetic goods, such as hair dyes, which can penetrate the skin and hair roots to enter the body. Because of this, they can result in a number of health issues if they are present in the body in high amounts[3]. Thus, it is more crucial to use many types of hair dyes from different manufacturers to ascertain the heavy metal level of each product. Commercial hair color formulae are complicated, containing dozens of ingredients and formulas that vary from manufacturer to manufacturer. Chemical dyes, antioxidants, modifiers, alkalizes, ammonia, soaps, fragrances, wetting agents, and a host of other chemicals are typically found in

small quantities in hair color products. These ingredients are used to give the color a desired process, such as increasing or decreasing its durability, or to transfer special qualities to hair, like softening the tissue. Chemical ingredients for hair dye typically have names like 4-amino-2-hydroxytoluene and m-Aminophenol and contain amino compounds. Pigments made of metal oxides, such as iron oxide and titanium dioxide, are widely utilized[4].

Hair color has been found to be a source of heavy metal contamination. The degree to which hair coloring alters the number of heavy metals in hair varies per element[5]. Scientists have long speculated that hair dye, especially darker-colored brands, may be linked to cancer. In fact, frequent use of hair color has been linked to an increased risk of multiple myeloma and non-Hodgkin's lymphoma, according to some research. Up until today, the results of numerous research that linked hair dye to cancer were typically conflicting and ambiguous[5].

A recent study that was published in the American Journal of Epidemiology suggests that women who have colored their hair for a long time may be more susceptible to non-Hodgkin's lymphoma, a lymph system cancer that kills about half of its victims. Preservatives, fragrances, propylene glycol, sodium ethylenediaminetetraacetic acid (EDTA), paraphenylenediamine, and resorcinol are the principal components of the dye. PPD, or paraphenylenediamine, is the primary toxin that causes poisoning[6]. Since lead acetate is used as a color additive in "gradualist" HDPs, PTEs have the potential to seriously damage enzyme systems, increase the production of free radicals, and displace or combine them with necessary components of metalo-enzyme mixtures, as well as combine them with nutritional mineral imbibition's. To provide a gradual coloring effect, these materials are applied over a predetermined amount of time[6].

Any substance or preparation intended to come into contact with the teeth and mucous membranes of the oral cavity, as well as the various parts of the human body (epidermis, hair

system, nails, lips, and external genital organs), with the sole or primary goal of cleaning, perfuming, altering the appearance, correcting body odors, protecting, or maintaining them in good condition, is considered a cosmetic product[7]. These are materials meant to be applied in various ways to the human body or any portion of it, such as rubbing, pouring, spraying, or sprinkling, in order to clean, beautify, enhance attractiveness, or change appearance[7]. This description encompasses a wide range of items used by both sexes, including deodorants, infant products, hair creams, skin-care creams, lotions, powders and sprays, fragrances, lipsticks, fingernail polishes, eye and face cosmetics, permanent waves, hair colors, and mouthwashes.

The application of cosmetics to enhance one's physical appearance is a millennium-old global custom. Despite difficult economic times, people's awareness of the desire to enhance their physical appearance and the dramatic growth in product marketing in print and electronic media have led to a global surge in demand for cosmetic products[4]. Across all social classes, cosmetics use is a regular form of self-care[5]. Metallic impurities in cosmetics can come from two sources: either as contaminants resulting from the manufacturing processes, or as ingredients, like zinc oxide in sunscreen creams, inorganic mercury compounds in skin-lightening creams, lead acetate in progressive hair dyes, and aluminum and zirconium salts in antiperspirants[6]. Annex II of Directive 76/768/EEC of the European Union prohibits the intentional use of compounds of antimony (Sb), arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), and nickel (Ni) as ingredients of cosmetic products because they are deemed unsafe due to toxicity issues. Despite this prohibition, these compounds are still present in cosmetic products today due to their ubiquitous nature and contamination from production processes[8].

There are two main reasons why the presence of metals in cosmetic products is concerning:

i. The consumption of cosmetics may be a potential daily and frequently long-term source of exposure for the general public to metals in cosmetics[8].

ii. Many of them have been linked to various long-term health consequences, including hair loss, cancer, brittle hair, dermatitis, reproduction issues, and developmental, neurological[9].

Certain metals are strong respiratory poisons and endocrine disruptors. Furthermore, certain metals, including Cr, Ni, and Co are well recognized skin sensitizers, while others, like As, Sb, As, Pb, Hg, and Hg, are extremely poisonous and have a wide range of cumulative health impacts[10]. These factors have led to increased regulatory scrutiny of the cosmetics industries worldwide, with the shared goal of ensuring safe chemical concentrations in these products[11]. The amount of money spent on hair beauty enhancements reflects the attention that is paid to hair appearance in today's world. However, these findings are particularly relevant to people with hair diseases. A significant instrument for improving patient adherence to scalp treatments is hair cosmetics, given the variety of hair kinds and ethnicities.

Trueb defines them as "medications intended to come into contact with the hair and scalp, with the purpose of cleansing, improving appearance, altering appearance, and/or protecting them to maintain their health"[12]. Two primary categories can be identified for hair cosmetics:

i. Hair care products that have a transient effect, such as sprays, shampoos, conditioners, and temporary hair color.

ii. Cosmetics such as relaxers, bleaches, waves, and colors that leave a lasting impression on the hair shaft.

PTEs are among the most significant environmental pollutants; some of them may be hazardous to human health even at extremely low concentrations because to their lengthy biological half-lives, non-biodegradability, and toxicity[10]. Heavy metal exposure occurs to people on a regular basis in a variety of ways. As a result, it might be among the health issues affecting people. These substances enter the human body through both natural and man-made activities, releasing them into the environment. When these substances enter the body, they can cause a variety of issues, including cancer, birth defects, allergic reactions, contact dermatitis, brittle hair, and hair loss, as well as neurological and developmental disorders, reproductive disorders, cardiovascular diseases, skeletal, blood, immune, and gastrointestinal disorders[11]. Regretfully, no research has been done on the amounts of these dangerous substances in chemical hair dyes that are sold in Ibadan. Determining the carcinogenic effects of these trace potentially harmful substances on hairdressers is crucial since they are frequently included in hairdressing cosmetics, which are common raw materials in the hairdressing business.

1.2 Statement of the Problem

PTEs are among the most significant environmental pollutants; some of them may be hazardous to human health even at extremely low concentrations because to their lengthy biological half-lives, non-biodegradability, and toxicity[10]. Heavy metal exposure occurs to people on a regular basis in a variety of ways. As a result, it might be among the health issues affecting people. These substances are discharged into the environment by both man-made and natural processes. When these substances enter the human body, they can cause a variety of issues, including cancer, birth defects, allergic reactions, contact dermatitis, brittle hair, and hair loss. They can also cause neurological and developmental disorders, reproductive issues, cardiovascular

diseases, skeletal, blood, immune, and gastrointestinal disorders[11]. Regretfully, no research has been done on the amounts of these dangerous substances in chemical hair dyes that are sold in Ibadan. Determining the carcinogenic effects of these trace potentially harmful substances on hairdressers is crucial since they are frequently included in hairdressing cosmetics, which are common raw materials in the hairdressing business.

1.3 Justification of the Study

There is little information about PTEs in HDPs in Ibadan, Nigeria. The significance of this research lies in the fact that hair stylists, barbers, and individuals in Ibadan and throughout the nation can utilize the information to help them make decisions about hair coloring and HDPs. Also, given the study's results will provide consumers and legislators information on the amount of PTEs in HDPs, they will be crucial. One of the hottest trends in beauty right now is hair coloring, which needs to be done as safely as possible to guarantee that the finished goods live up to international standards. Finally, because it advances our understanding of the role that environmental scientists and other researchers can play in disseminating best practices to lower PTEs in HDPs, the study is significant to them[12].

1.4 Aim and Objectives of the Study

The purpose of this study is to identify the PTEs that are present, their concentrations, and the health risks associated with them in a few locally sourced hair color products.

The main objectives of the study are to:

i. use Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) to ascertain the presence and concentration of specific PTEs (Ag, As, Boron, Cerium, Cadmium, Cobalt, Chromium, Cesium, Copper, Iron, Mercury, Magnesium, Manganese,

Molybdenum, Nickel, Palladium, Lead, Sulphur, Antimony, Selenium, Silicon and Zinc) in a few popular chemical hair coloring brands.

ii. determine the extent of exposure that adults' inhabitants of Ibadan have to these PTEs and, in turn, the associated non-carcinogenic (hazard quotient and hazard index), life cancer risk health risk associated.

1.5 Significance of the Study

This study is crucial for protecting public health, improving regulations, and promoting safer cosmetic products**.** By identifying toxic elements in hair dyes, it empowers consumers, influences policymakers, and encourages manufacturers to adopt safer practices. PTEs from hair dyes can enter wastewater, contaminating water sources and soil. The study highlights the need for eco-friendly disposal methods and sustainable production. Many hair dyes, especially locally produced or low-cost products, may contain toxic metals (e.g., lead, arsenic, cadmium, mercury) that pose serious health risks. Chronic exposure to PTEs can lead to skin irritation, allergies, organ damage, neurological disorders, and even cancer**.** This study helps identify hazardous products, raising awareness among consumers and healthcare providers. Many users are unaware of the toxic ingredients in hair dyes, assuming they are safe. Findings from this study can educate consumers about potential risks, encouraging them to choose safer alternatives or demand better product labeling. Helps align local product safety standards with international guidelines (e.g., WHO, FDA, EU Cosmetics Regulation). Provides scientific data for policymakers to establish maximum allowable limits (MALs) for toxic elements in cosmetics.

1.6 Scope of the Study

Although the amount of potentially hazardous ingredients in many cosmetics items will be extremely valuable to consumers, only hair care products namely, Cruset (black dye), Tovchcolor (green dye), Subaru (gold dye), Subaru (white dye), and Subura (wine red dye) were examined in this study. This restriction results from the research project's time constraints as well as the availability of other hair care product kinds in the chosen sourcing area, which is Ibadan, Nigeria. Raw material origins, prospective industrial sources, and matrix effects brought about by product processing were not taken into account. Only the ICP-OES and GC-MS were used for this study due to time constraints and the availability of alternative technologies for sample analysis.

1.7 Limitation of the Study

The study used standard risk assessment models (e.g., Hazard Quotient, Cancer Risk) with assumptions about exposure frequency, skin absorption rates, and body weight, which may not reflect real-world usage. Variations in individual susceptibility (e.g., skin sensitivity, genetic factors) were likely not considered. The health risk assessment may be based on short-term exposure models, whereas hair dye use is often a repeated, long-term exposure scenario. Chronic health effects (e.g., cancer, endocrine disruption) may not be fully captured.

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Chapter Two

Literature Review

2.1 Hair

The integrated system that is hair exhibits unusual chemical and physical properties. It is a multi-part morphological structure that functions as a single entity. Mammals' hair shafts are separated into three primary sections: the cuticle, cortex, and medulla. The medulla is lacking in children's fine hair and present in corser hair, such as thick, beard, and grey hair. Asians have coarser hair than Caucasians, and their hair contains more medulla. Since the medulla creates a region of weakness and a conduit for cracks to spread along the fiber's axis, it may be involved in the splitting of hairs[1].

The cuticle, which resembles roof shingles and is composed of flap-overlapping scales called keratinocytes, is a chemically resistant area. The differential friction effect in hair is caused by the orientation and form of the cuticle cells. Asians typically have 7-8 centimeter-thick cuticles, Caucasians have slightly thinner cuticles, and African hair has even thinner cuticles. African hair is more likely to break as its cuticle layer is thinner there. The epicuticle, a thin proteinaceous membrane found in each cuticle cell, is coated in a lipid layer that comprises free lipids and 18-Methyl Eicosanoic Acid (18-MEA)[2].

Three layers, the A-layer, the exocuticle or B-layer, and the endocuticle, lie beneath the membranes of cuticle cells. They are all strongly cross-linked proteins, primarily cystine. Cysteine content is greatest in the first one and lowest in the third. Hair that has been treated with alkaline chemical cosmetic operations may become more hydrophilic as a result of the elimination of 18-MEA, which is what gives hair its hydrophobic properties[3].

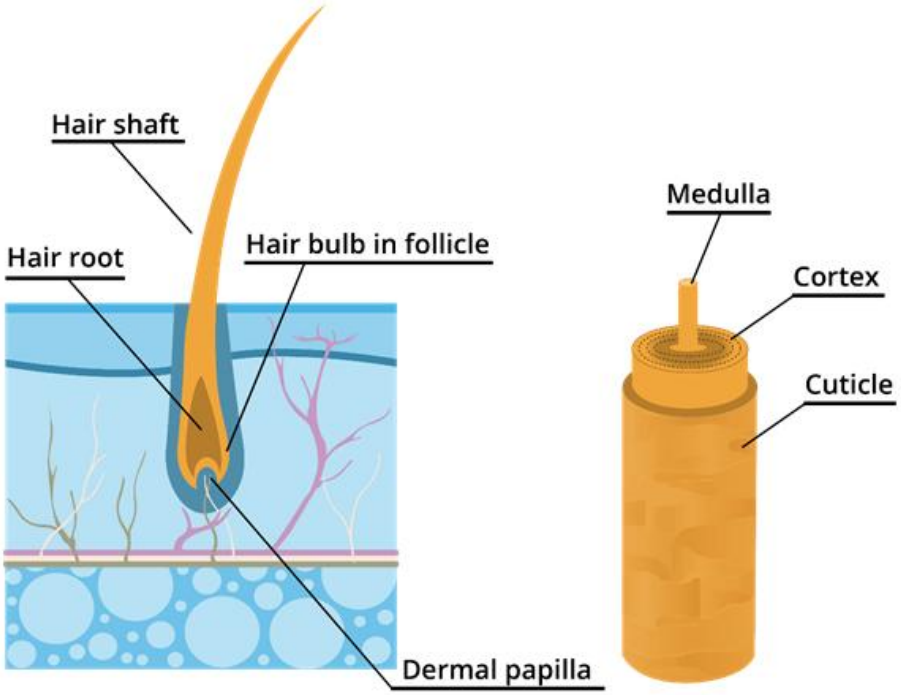


Figure 2.1: Hair Follicle Anatomy
Source[3]

2.1.1 Cell Membrane Complex (CMC)

The term "cell membrane complex" (CMC) refers to an intercellular matter that is made up of cell membranes and an adhesive material called cement that binds the cell membranes between two cuticle cells, two cortical cells, and cuticle-cortex cells. The beta-layer, which is the most significant layer of the CMC, is called the intercellular cement and is surrounded by other layers from each cell. The CMC and the endocuticle are extremely vulnerable regions to chemical treatments like bleaching, dyeing, and hair straightening/permanent procedures. Additionally, the friction from routine grooming and shampooing may disturb the CMC[4].

Prior to the hair fiber rupturing, CMC fractures may be visible. The cell surface becomes less hydrophobic and more hydrophilic, negatively charged, as a result of repetitive rough washing, unprotected drying, friction, sunshine, and alkaline chemical treatments. A decrease in lipid content also occurs[2,4].

The majority of the mass of human hair is made up of the cortex, which is composed of melanin and protein granules and is formed of elongated, fusiform cells connected by a CMC. Additionally, the cortical cell contains spindle-shaped fibrous structures known as macrofibrils. Microfibrils, which are highly structured fibrilar units and matrix, make up each macrofibril. High cystine content crystalline proteins create the matrix. The arrangement of the macrofibrils is spiral-like. Protofilaments, which are subfilamentous units found inside microfibrils, are made up of short segments of alpha-helical proteins coiled into polypeptide chains. Chemical forces such ionic forces, hidrogene bonds, Van de Waal forces, and disulfide bonds keep the alpha-helix coiled. The method of straightening hair involves releasing the tensions that confine the coil, enabling it to be expanded. Hair swelling and highly alkaline chemicals (pH greater than 9.0) such as guanidine, ammonium thioglicolate, sodium or lithium hydroxide are involved in the

reduction process of the hair. All of them may result in splits or cracks in the CMC and the endocuticle, but the primary cause of hair damage following the use of hair reducing products is actually improper usage of the products and carelessness when combing hair when it is reduced[3]. By using hair care products correctly, hair damage from chemical processes can be reduced, prevented, or restored. Hair cosmetics can reduce electrical charges and friction forces, fortify the cuticle, and increase the hydrophobicity of hair[3,4].

2.2 Types of Human Care Products (HCPs)

Hair care professionals assist in managing the characteristics and actions of hair, enabling it to be styled and maintained in a desired way. Hair conditioners, hair sprays, relaxers and straighteners, permanent waves, shampoos, rinses, tonics, and dressings can all fall under this category[3,4].

2.2.1 Hair Coloring Products

A number of the most reactive compounds used in the cosmetics sector are found in hair coloring products and hair dyes. Permanent oxidative dyes and temporary or semi-permanent direct dyes are the two categories of hair coloring products. Resorcinol, aminophenol, and paraphenylene-diamine (PPD) are examples of dye intermediates found in oxidative hair dyes, along with the oxidant hydrogen peroxide[4]. Since couplers allow PPD to be oxidized and produce colorful reaction products, it is an aromatic chemical that is commonly employed in practically all hair coloring formulations. Permanent and transitory dyes are examples of direct dyes. As opposed to semi-permanent hair dyes, which contain nitro-aminophenols, nitro-phenylenediamines, triphenylmethane, and some azo dyes, temporary hair colors contain anthraquinone, azo, and other dyes[4]. In contrast to semi-permanent or temporary hair dyes, permanent hair dyes are composed of two ingredients that are combined prior to usage, producing the dye on or in the

hair through a chemical reaction. Studies reveal that PPD is a common allergy in humans, despite the benefits of utilizing it in hair color and dyes. Reports exist of contact sensitization brought on by PPD. A portion of these cases are linked to the paragroup's hypersensitivity or the production of oxidized compounds as a result of PPD's oxidation by air exposure. PPD's propensity for sensitization is influenced by N-Substitution. Additionally, the sensitization potential is often influenced by the length of the alkyl substituent's chain. Other kinds of dyes exist as well, like natural and metal salts. Whereas natural dyes use "henna" as their only dye ingredient, metal salts are primarily used to conceal graying hair and are typically based on lead acetate[5].

Numerous groups have investigated the genotoxicity of different permanent hair dye ingredients; their findings and outcomes have often been inconsistent. For instance, the ability of six significant phenylenediamines (PDs) to cause different genotoxic end points was assessed in relation to their genotoxicity. For every end point examined, no single PD was found to be favorable or negative. Animal studies on the reproductive toxicity of PPD and other PDs have also been conducted. There is no proof that exposure to these substances causes' negative effects on the reproductive system[5].

Numerous epidemiological studies have suggested that high exposure to hair dyes may put some occupational groups, such as beauticians and hairdressers, at risk for cancer. Hueber-Becker's latest investigation, however, did not find any indication of an elevated risk of neoplastic disease[6]. The current consensus is that handling hair colors safely and with personal protective equipment (gloves, for example) can shield users including professionals from harmful health consequences.

2.2.1.1 Hair Dyes

Many hair color varieties are categorized based on how deeply they penetrate the hair shaft or its surface. They consist of;

2.2.1.1.1 Temporary Hair Dyes

Shampoos, lotions, and foam are administered as temporary coloring agents. The color of the hair is altered for a brief period of time typically up until the first wash. Typically, they are used to cover up a few graying hairs, add color highlights, and eliminate yellowish tones from white hair. High molecular weight chemicals that merely deposit on the hair's cuticle and are readily removed are the ingredients of temporary colors. In order to decrease its solubility and boost its affinity for hair, the dye is linked to a cationic polymer. To create the finished product, the resultant complex is dissolved in a base using surfactants[7]. Henna, which is applied to the skin and nails and is derived from the plant *Lawsonia alba,* is one example. Research have revealed a few instances of henna-related allergic contact dermatitis[7].

2.2.1.1.2 Semi-permanent Hair Dyes

Ingredients such as low molecular weight aromatic dyes or nitro-aromatic amines are used to create semi-permanent hair colors. These dyes are water soluble and do not oxidize, thus they can be removed after six to ten wash cycles or sooner. They don't include ethanolamine or ammonia, although they might contain resorcinol or hydrogen peroxide[7]. Semi-permanent coloring can't lighten hair; its primary goal is to add additional tone to the natural hue. Low molecular weight is a crucial feature that allows these chemicals to permeate into the intermediate cuticle layers without forming a strong bond with the hair protein itself[7].

Consequently, there is no need for any previous hair modification before using semi-permanent colors.

2.2.1.1.3 Permanent Hair Dyes

Through the process of oxidation, permanent hair coloring modifies the color of the hair. Infusing the hair with color is made possible by this. In addition to being resistant to external factors, such as washings, permanent colors allow for the darkening or lightening of hair color for 4-6 weeks. In addition to covering the greatest number of gray hairs, they provide a wide variety of colors. The concept involves coloring molecules penetrating hair shaft pores that have previously been enlarged through hydration and alkalinization. The molecule now undergoes oxidation and takes on color, which is transferred to the cuticle and cortex's keratin to resemble naturally occurring melanin granules[7]. Some intermediates are produced during these processes; these are typically derivatives of p-phenylenendiamine (PPD), which gives rise to dark brown and black hues, or p-aminophenol, which gives rise to blonde hues.

Although resorcinol was once also present in several dyes, many businesses removed it for security-related reasons. PPD is a hapten, or incomplete antibody stimulating chemical, that can bind with a skin protein molecule to cause sensitization, which can trigger an allergic reaction upon subsequent application. PPD-related allergic skin responses can vary in intensity and occasionally affect the mucosae. For these reasons, before applying the coloring agent to the scalp in individuals who may be sensitized to PPD, a skin allergy test must be performed at least 48 hours in advance[8]. As previously indicated, dyes also contain active components such as ammonia, an alkalizer, and hydrogen peroxide, which oxidizes the dye molecules and bleaches out the original hue. Additional additives include solvents that aid in improving the viscosity and solubilization of the dye, surfactants that remove oil and sebum from the hair surface, and

chelating agents that preserve chemically stable peroxide and its activity, deactivating any catalytic metals in the solution. Certain dermoscopic diagnoses of hair disorders may be hampered by dyes[8]. Permanent dye, for instance, can enter hair follicles and give the characteristic "black dot" look associated with alopecia areata; semi-permanent dye, on the other hand, might deposit on the scalp and simulate excoriated lesions or sun exposure. Dye exposure for an extended period of time can result in contact dermatitis, which can lead to telogen effluvium but, in extreme circumstances, can cause face edema. Table 2.1 provides a summary of the most widely used hair color products[9]. As previously indicated, PPD is an incredibly strong contact sensitizer that is permitted in hair dyes at concentrations up to 6%. Additional common allergies linked to hair color include toluene-2,5-diamine, which is safe to use at concentrations up to 10%, p-aminophenol, and m-aminophenol, which is safe to use at concentrations up to 2%. Nine persons may develop allergic contact dermatitis from hair color products that include PPD or one of its specific derivatives, according to a study. According to this study, patients may have dermatitis from hair dye at quantities below those allowed by the EU Cosmetic Directive[9].

Another intriguing study ranked the likelihood of contact allergies and examined the predictions made for the sensitization potential of 229 different substances found in hair dyes. The results showed that approximately 75% of all hair dyes were predicted to be strong or moderate sensitizers even stronger than PPD and that many of these are not currently used to diagnose contact allergies to hair dyes. Toluene-2,5-diamine has been found to be less potent than PPD, although resorcinol appears to be less potent than PPD. Just 22% of hair color ingredients were expected to be weak sensitizers, and 3% were expected to be either completely non-sensitizing or incredibly weak[10].

A new European hair cosmetics series was recently created after a study gathered comprehensive data on the usage of hair cosmetics as of right now. They gathered all known allergens that are significant for patients with contact allergies to hair cosmetics, as well as allergens that are less significant. This emphasizes the necessity of assessing these compounds in specialized departments and establishing a network for cosmetovigilance[11]. Bleaching agents: these products, which include hydrogen peroxide, ammonia, and persulfate salts, permanently lighten hair without the need for coloring.

A sequence of color phases makes up the labor-intensive procedure. Hydrogen peroxide, as previously discussed, bleaches off the hair's natural color. Once the cuticle's scales are raised, the oxidizing agent in an alkaline solution enters the hair's cortex and chemically alters the melanin. As a result, the melanin granules dissolve and leave microscopic gaps in the cortex[11]. Because of this, frequent bleaching treatments may result in permanent elevated scales and increased porosity in the hair, which can cause weathering of the hair. Although the precise immunological mechanism causing rhinitis, asthma, contact urticarial disease, and even anaphylaxis can be triggered by persulfates, it is currently unknown[11].

Table 2.1: Summary of Most Commonly Used Hair Dyes

Types of hair dyes	Level of Penetration	Main Ingredients that may be found in these Hair Dyes
Temporary	Cuticle	*Lawsonia inermis*, lawsone, PPD, henna
Semi-temporary	Cuticle	hydrogen peroxide, resorcinol, PPD, para-toluenediamine, para-aminophenol
Permanent	Cortex	Ammonia, ethanolamine, PPD, para-toluenediamine, or para-aminophenol, resorcinol, m-aminophenols

Source[9]

2.2.1.1.4 Shampoos

Shampoos protect the hair shaft from damage in addition to cleaning the scalp. Addition of active chemicals to shampoo formulations also treats a number of scalp ailments. Regardless of the illness or condition (dermatitis, seborrhea, alopecia, psoriasis), it is preferable that the hair strands be kept aesthetically pleasing by maintaining their softness, combability, and gloss while treating the scalp[11]. Although products with as few as four ingredients are available, shampoos usually consist of 10–30 ingredients. The products are categorized as follows:

i. Agents for cleaning
ii. Components that improve the product's comfort and stability
iii. Conditioning chemicals that add luster and softness, lessen flyaway, and improve the product's capacity to disentangle.
iv. Specialty compounds meant to address particular issues like oily hair and dandruff[11].

The following conditions are primarily impacted by using strong shampoos: Frizz and difficulty detangling hair strands. The primary cause of frizz, attrition, can be reduced with proper cleaning product formulation. Conversely, fiber attrition is worsened if the shampoo formulae lack the necessary content[11]. Shampoos can result in contact dermatitis, despite being regarded as safe products. Typical allergens found in shampoos are:

i. Propylene glycol
i. Vitamin E (tocopherol)
ii. Methylchloroisothiazolinone
iii. Formaldehyde-releasing preservatives
iv. Parabens
v. Benzophenones Cocamidopropyl betaine

A shampoo's ability to extract oil and debris from the hair shafts and scalp is made possible by surfactant agents; nevertheless, the degree of cleansing action required to prevent total elimination of the skin's natural oils and sebum must be moderate. Because modern shampoos have a brief contact time with the scalp, they are gentle on skin and mucous membranes, and contact dermatitis rarely develops as a result. Shampoos typically contain foaming agents and detergent agents to keep insoluble soap from building up on the scalp and hair. Because of their molecular makeup, surfactant agents are the most significant cleaning ingredients in shampoos. Specifically, one end of the molecule is negatively charged and soluble in water, meaning it does not mix with oils; the other end is soluble in both oil and grease and does not mix with water. These molecules encircle the grease fragments that are localized on the hair and scalp; the water-soluble parts stay outward and the oil-soluble parts go into the grease, forming a hydrophilic mass that is completely negatively charged; the hair shaft's surface has negative charges that tend to push the mass's negative charges apart, which reduces the tension between water and grease on the surface and produces foam that incorporates the dirt, preventing it from coming back on the hair and scalp.

Shampoos' conditioning molecules combine the cleaning activity with the purpose of giving hair manageability, shine, and antistatic qualities. The fatty ingredients in these conditioning shampoos such as silicone, vegetable oils, wax, lecithin and lanolin derivatives, collagen, animal proteins, quaternium ammonium compounds, or cationic polymers reduce the friction caused by combing the hair and, consequently, the risk of hair shaft damage[12]. A crucial factor to take into account is the pH of the shampoo. A lot of them have an alkaline pH, which makes the hair shaft swell and makes the hair more vulnerable to damage. For hair that has been chemically treated due to permanent dyeing or permanent waving, a neutral pH shampoo is the best option[12].

Additional additives include of antioxidants like ascorbic acid and α-tocopherol as well as UV absorbers such derivatives of benzophenone. Shampoo preservatives, which include parabens, tetrasodium EDTA, ethylenediaminetetraacetic acid (EDTA), and sodium benzoate, work to stop bacteria from growing. In addition, the majority of shampoos include additional components including humectants like sorbitol and glycerin, dyes, scents, pearlishing agents, and moisturizers such fatty acid esters and natural oils. "Medicated" shampoos are made with active components that are specifically chosen to treat medical diseases, primarily psoriasis and seborrheic dermatitis[11].

Ketoconazole, ciclopirox olamine, zinc pyrithione, piroctone olamine, tar derivatives, salicylic acid, poly-vinyl-pyrrolidone, selenium sulfide, iodine complex, menthol, and colloidal sulfur are among the active components. The advantages of cosmetics combined with the effectiveness of medicinal agents are made possible by the integration of cosmetic technology and medical therapy. Shampoo-related side effects are uncommon. Accidental contact with mucous membranes, like those in the nose and eyes, is the most frequent.

2.2.3 Surfactants

Table 2.2 shows surfactants as cleaning products that have taken the place of soap. By decreasing the physicochemical adhesion forces that bind residues and contaminants to the hair, they exert their effect. These contaminants are dissolved by surfactants, which stops them from attaching to the scalp or shaft. The type and quantity of surfactants a shampoo uses, along with how successfully it removes grease, determine how cleaning it is[12]. Sebum, or non-soluble fats, are known as residues because they don't dissolve in water. Surfactants have a hydrophobic and a hydrophilic molecular part that must be eliminated from the hair shaft. While the latter will make a chemical bond with the water, the former will form a bond with the fat. A polar head and a

chain of fatty hydrocarbons (tail) make up the majority of surfactants[13]. When surfactants come into contact with water, they form a micelle structurally. Their shape becomes spherical, with an inner that is hydrophobic and where the fats and residues are bound, and an exterior that is hydrophilic and washable with water[13]. The surrounding water molecules attract the ionic ends of the surfactant when enough shampoo molecules have buried their hydrocarbon ends in the particle. After that, the particle is suspended in water and becomes emulsified. This type is one that can be washed off[13]. The four types of surfactants are anionic, cationic, amphoteric, and nonionic, based on the electric charge of the polar extremity.

Table 2.2: Classification of the Shampoo Surfactants

Class	Example	Characteristics
Anionic	Ammonium lauryl sulfate, sodium laureth sulfate, sodium lauryl sarcosinate, sodium myreth sulfate, sodium pareth sulfate, sodium stearte, sodium lauryl sulphate, alpha-olefin sulfonate, ammonium laureth sulphate	Deep cleansing
Cationic	Trimethylalkylammonium chlorides, and the chlorides or bromides of benzalkonium and alkylpyridinium ions	Hair softener. Mild cleansing
Nonionic	Fatty alcohols, cetyl alcohol, stearyl alcohol, and cetostearyl alcohol (consisting predominantly of cetyl and stearyl alcohols), and oleyl alcohol	Mild cleansing Some considerations about the eco-system
Amphotheric	Alkyl iminopropionates and (amido) betaines	Do not irritate the eyes. Moderate cleansing

Source[12]

2.2.3.1 Anionic Surfactants

The hydrophilic polar group of anionic surfactants is negatively charged. Anionic surfactants include sodium lauryl sulfate, sodium laureth sulfate, sodium lauryl sarcosinate, sodium myreth sulfate, sodium pareth sulfate, sodium stearte, sodium lauryl sulfate, and alpha-olefin sulfonate. Anionic surfactants are strong cleaners that can produce electrical negative charges on the surface of hair and promote frizz and friction, even if they are excellent at eliminating sebum and grime. Other surfactants, referred to as secondary surfactants, such as nonionic and amphoteric surfactants, are added to the mixture to reduce damage[14].

2.2.3.2 Cationic Surfactants

A positively charged hydrophilic end is present in cationic surfactants. The chlorides or bromides of benzalkonium and alkylpyridinium ions, as well as trimethylalkylammonium chlorides, are typical examples. Since they all include a quaternary ammonium ion, they are all examples of quats. Frizz is usually reduced and the negatively charged net of the hair surface is neutralized. They are frequently employed as shampoo softeners[14].

2.2.3.3 Nonionic Surfactants

There is no electric charge in non-ionic surfactants. Because of the non-dissociable nature of their hydrophilic group, they do not ionize in aqueous solutions. Many long-chain alcohols have certain characteristics of surfactants. The fatty alcohols, cetyl alcohol, stearyl alcohol, cetostearyl alcohol (which is primarily made up of cetyl and stearyl alcohols), and oleyl alcohol are prominent among them[14].

2.2.3.4 Amphoteric Surfactants

The pH of the solution affects the charge of the hydrophilic portion of amphoteric surfactants. As a result, they can function as cationic surfactants in acidic solutions or anionic surfactants in alkalic ones. They are incredibly gentle and have great dermatological qualities. Amphoteric substances can be divided into two categories: (amido) betaines and alkyl iminopropionates[14].

2.2.4 Conditioners

Conditioners are used to increase combability, reduce frizz, detangle hair, and reduce friction. Conditioners work by lubricating the cuticle, which lessens the hydrophilicity of the fiber, and by introducing positive charges to the hair fiber to balance its electrical negative charge. They contain lubricating and anti-static materials that fall into five major categories: hydrolyzed amino acids, oils, waxes, polymers, and cationic molecules[15]. Silicone is the most often utilized and active conditioner agent[39]. Different silicone kinds have varying capacities for deposition, adhesion, and wash-out, which will affect how well the conditioner performs[15].

The functions of the conditioners include;

i. Improve combability
ii. Mimetize the hair natural lipid outer layer: 18-MEA
iii. Restore hydrophobicity
iv. Seal the cuticle
v. Avoid or minimize frizz, friction: Neutralize the negative charged net
vi. Enhance shine, smoothness and manageability.

2.2.5 Silicones

Silicones are inert, heat-resistant, hybrid (inorganic-organic) polymers that resemble rubber and are generated from crystal quartz. Silicones are first made from silica (silicon dioxide), which is

found in sandstone, beach sand, and other natural elements. The most common silicone in the hair care market is dimethicone, and entropy plays a key role in how well it adheres to the surface of hair. The primary component of the two-in-one shampoos is dimethicone. Among others are siloxysilicates, anionic silicones, aminosilicones, and others. They act differently on the hair because of differences in their solubility and deposition in a water medium. By reflecting light, certain silicones can even improve the sheen of hair fibers. While siloxysilicates give hair more substance, dimethicone shields the hair shaft from harsh forces[16].

Heat damage can be avoided and raised cuticle scales can be re-cemented with polysiloxane polymers. Depending on the molecule size and system charge, amino functional silicones may or may not be more substantial to the hair than dimethicone despite being cationic substances. Because dimethicones are hydrophobic, they absorb better at the roots of hair than at the tips. The products use cationic bridging agents to increase the affinity between the silicone and the hair, improving the deposition of dimethicone on chemically treated and damaged hair[17].

Additional polymers include proteins and polypeptides, which are significant to hair because they have a lot of polar and ionic bonding sites and are big molecules that adhere to the surface of the hair (van der Walls force). Even smaller molecules (less than 1000 Da) can permeate hair, particularly in cases of hair damage. It has been demonstrated that protein hydrolysates, especially those with low molecular weight distribution, can shield hair from environmental and chemical harm. Keratin hydrolysates made from wool, horns, and nails are among the many varieties of protein hydrolysates from plants and animals that are utilized in hair and personal care products[16]. Lately, hydrolyzed hair keratin and feather keratin peptides have been obtained by enzymatic hydrolysis utilizing Bacillus spp. in submerged fermentation. The majority of these hydrolysates are acquired by chemical hydrolysis and hydrothermal techniques. The feather-

derived hydrolyzed protein was applied to the cuticle scales, aiding in cuticle sealing, particularly when the hair was heated with a flat iron, and enhancing the color and gloss of the hair[16]. Particularly after bleaching, chemically treated hair deposited more protein. Given the positive charge of the hydrolyzed amino acids, it is plausible that the negatively charged hair attracts positively charged molecules, which balance the electrical charges and reduce frizz and friction17. Typically, keratin-containing animal parts like feathers, horns, hooves, hair, and wool are gathered from discarded materials to make keratin hydrolysates. In order to replicate the natural makeup of keratin, certain companies have created products that contain a complex of non-animal free amino acids extracted from wheat, corn, and soy proteins. However, due of its mechanical and protective qualities, keratin is an irreplaceable protein, and utilizing amino acids will not fix or rebuild the damaged molecular structure[17].

2.2.6 Other HDPs: Mineral and Vegetable Oils

The impact of vegetable and mineral oils on human hair is a topic covered in relatively few published studies. The hydrophobicity of the oil is the primary physical characteristic of this class of components. Compared to polyunsaturated oils, saturated and monosaturated oils penetrate into the hair considerably better. Oils are essential for shielding hair from harm. Certain oils have the ability to permeate hair and lessen the quantity of water that is absorbed by the hair, which lowers swelling[18]. Reduced hygral fatigue repeated swelling and drying may be the outcome, and this can harm hair. By filling the spaces between the cuticle cells, oil can stop hostile chemicals like surfactants from entering the follicle. Regular application of oil can improve the shaft's lubrication and help stop hair breakage. An investigation saw research on the effects of mineral oil, coconut oil, and sunflower oil on hair by Rele and Mohile[19].

Out of three types of oils, only coconut oil was discovered to lessen the loss of protein in hair, regardless of damage, when applied as a pre- and post-wash grooming product. Mineral and sunflower oils don't lessen the loss of protein in hair. The variations in the outcomes could be attributed to the makeup of each of these oils. Being a triglyceride of lauric acid, or main fatty acid, coconut oil has a strong affinity for hair proteins and can enter the hair shaft due to its straight linear chain and low molecular weight. Mineral oil is a hydrocarbon that is impermeable. With its large structure, double bonds, and restricted penetration into the fiber, sunflower oil is a triglyceride of linoleic acid that does not reach the cortex. In order to prevent hair damage, the mineral oil and sunflower oil may have a film effect and adsorb to the cuticle's surface, increasing shine and reducing friction[20].

The impact of mineral oil, coconut oil, olive oil, and sunflower oil on hair was studied in 2019[21]. With the exception of mineral oil, heat reduced the capillary adherence of the other oils because they were able to diffusely penetrate the hair fiber and leave a thin coating on the outside. Thick layers of oil may give the hair an oily, heavy appearance even though they can conceal the cuticle's raised scales. Oils that penetrate well into the fiber and leave a thin film on the surface should be reapplied. Brazilian butters and oils were researched in 2018[21]. The following materials were examined: tucumã (48% lauric acid and 27% myristic acid), ucuúba (75% myristic acid), passion fruit seed (77% linoleic acid), Brazilian nut (38% oleic acid and 35% linoleic acid), palm olein (47% oleic acid), buriti (79% oleic acid), palm stearin (42% palmitic acid and 41% oleic acid), ucuúba (35% myristic acid), and sapucainha (47% chaulmoogric acid, 27% hydnocarpic and 19 gorlic acid). In rainy situations, the combing force percentage was lowered by oil treatment. Poor combing was evident in the butter-treated hair, though. Oil-based hair treatments decreased the occurrence of split ends[21].

The lubricating actions of the oil on the fibers and water wetting work together to reduce combing forces. The combing force was enhanced by butters. When uncooked, butters are less pliable than oils and are difficult to distribute through hair strands. Combing force decrease was created by the Brazilian nut, passion fruit seed, palm oil, buriti, and mineral oils. Mineral oil cannot diffuse within the fibers of hair because it has no affinity for the proteins in hair. The primary benefits of mineral oil are improved gloss, easier combing, and a decreased likelihood of split ends due to its increased capacity to spread throughout the hair surface[22]. A study on the impact of oil films on moisture vapor on human hair was conducted in 2016 to examine the ability of oils to lower moisture absorption[23]. While mineral and fiber oils may not penetrate as much as coconut oil, both oils have a similar decrease in water sorption. Hair moisture recovery was enhanced by thickening the oil layer on the fiber surface.

The decrease in water pick up is caused by the oil that stays in the cuticle layer rather than the oil that enters the cortex. Moroccan argan oil, which is known for keeping hair hydrated and hydrophobic, has gained a lot of popularity as a key component in hair cosmetics. Argan oil from Morocco is currently the priciest edible oil worldwide. The most notable species in North Africa is the Moroccan native argan tree (Argania spinosa L. Skeels), valued for its social and botanical significance as well as its biological significance. Strong antioxidants, tocopherols and polyphenols, are abundant in the oil[22]. The kernels of argan fruits that have been sun-dried for a few days or up to several weeks are used to extract argan oil. The amount of time fruit is allowed to dry affects the extracted oil's quality[24]. There is a paucity of information regarding the advantages of Moroccan oil for hair care, despite the fact that scientific research supports its usage for long-term ailments including psoriasis and atherosclerosis due to its cardioprotective qualities[24].

2.2.7 Hair Styles

2.2.7.1 Permanent Waves

Hair may temporarily acquire a new "style" from the topical use of cosmetics in lotions or sprays, but this "style" will disappear after the first shampooing. A permanent alteration in the shape of hair requires a modification of the internal chemical structure of the hair through a specialized chemical process. The technique of creating a permanent wave involves employing chemicals to break and re-form the strong disulfide bonds in the hair shaft. After washing and wrapping the hair around a curler (the amplitude of which determines the thickness of the curl), an alkaline base waving lotion (ammonium thioglycolate is the most commonly used) is applied. This waving lotion raises the cuticle's scales and breaks the disulfide bonds that give the hair its natural shape by penetrating the cortex.

Following a predetermined amount of time, the waving lotion is rinsed off and a neutralizer which includes oxidizing agents like hydrogen peroxide is applied. This stabilizes the newly formed hair structure by rebuilding the disulfide bonds in a different order. Because of this, hair waving is the most hazardous cosmetic procedure for hair and needs to be done under close supervision. Bleached and permed hair frequently develops trichorrhexis nodosa. The cuticle cells become detached as a result of injury, exposing the cortex of the hair shaft. Little white knots that are visible to the unassisted eye are seen in the hair shaft. Because of breaking, the hair is short and brittle. When the hair shaft is examined under a microscope, one or more knots that break off readily to form two brush-like tips are visible.

2.2.7.2 Relaxers

The disulfide bonds in hair are broken, the shape of the hair is reformed, and new connections are formed as part of the relaxing mechanism. The hair goes from being wavy to being straight.

Tightly curled hair, like that of African Americans, may require multiple operations or extended exposure to the relaxer, resulting in weathering and breakage of the hair[25].

2.2.7.3 Hair Straighteners

In the past, the first hair straightening technique was used to African hair and involved putting hot irons or hot combs on the hair together with petrolatum-based oils to enable the device to glide over the hair and straighten the tresses. This kind of procedure keeps the fibers parallel by acting as cohesive and adhesive forces in a very viscous fluid, however it only results in temporary straightening. Straightening hair was initially done to make extremely coarse hair more manageable, but now days, straight hair is fashionable everywhere[25].

The permanent straightening effect is achieved with official hair straighteners, which are also known as chemical relaxers. 1–10% of alkaline straighteners' constituents include sodium hydroxide (a lye relaxer), lithium hydroxide, calcium hydroxide, or a combination of these, like calcium hydroxide and guanidine carbonate (no-lye relaxers).

The emulsion's high pH (9.0–14.0) causes the hair to swell and open cuticle scales, allowing the alkaline agent (OH) to enter the hair fibers and reach the endocuticle. The disulfide bridges are broken and rearranged when the straightening product comes into contact with keratin in the cortex, resulting in a pliable and stretched spiral keratin molecule[25]. It is not recommended to use chemical relaxers on the scalp since they may burn the skin. To avoid alkaline burns, it is advised to apply some petrolatum to the ears and along the hairline prior to applying the relaxer. Lanthionyl residues, a persistent thioesther crosslink, are produced when alkalis react with the cystine groups in keratin. It is referred to as "lanthionization" and involves substituting lanthionine for one-third of the cystine amino acid content while reducing peptide bond hydrolysis[5].

In order to realign the position of disulfide connections between newly formed polypeptide keratins, disulfide links are first broken with an alkaline reducing agent, followed by mechanical straightening of the hair using a comb during the reducing phase. Additionally, they interact with peptide bonds, hydrolyzing them to form acid and amine groups as well as residues of glutamic and aspartic acids. The relaxers must be rinsed off with running water after use on prewashed hair. They offer the longest-lasting hair straightening, but if done incorrectly, they can burn the scalp and break hair. Alkaline straighteners range in pH from 12 to above 13. Alkaline solutions cause the cuticle scales to expand and the fibers to swell in hair, which is sensitive to pH variations. This may weaken the hair's resilience and strength by making it more prone to friction[25]. It is necessary to repeat hair straightening at least once every 12 weeks. Only newly grown hair should be prioritized because several treatments can cause hair breaking, which typically happens where previously treated and newly grown hair meet. Excessive breakage can be avoided with careful application to new growth alone and prior conditioning of the hair.

The following side effects were most frequently reported following chemical hair straightening: split ends in just 17%, thinning and weakening of hair in 40%, dandruff in 61%, hair loss in 47%, and frizzy hair in 67%[26]. The phenomenon known as "supercontraction" generates enough stress to permanently straighten the fiber without the need for external forces or heat, such as a hot iron. In about 20 minutes, sodium hydroxide, a lye relaxer, can straighten hair. It was noted that the acquired hair length was substantially lower than predicted, despite the fact that hair relaxers are intended to increase length. Because of the super contraction effect, this might be the case[22]. When compared to alkaline relaxers that function with lanthionization, ammonium thioglycolate is another "no-lye" relaxer that can generate excessive fiber swelling but less supercontraction. Instead of completely breaking down the protein, this chemical reducing agent only weakens the

cystine connections in the hair. After that, a specific hydrogen peroxide solution needs to be used to oxidize (neutralize) the thioglycolate. Permanent straightening can be accomplished if a hot iron is used during the procedure. This serves as the foundation for the procedure known as "thermal reconditioning or Japanese hair straightening." Alpha-helical keratin proteins undergo "supercontraction" and change into amorphous proteins during thermal reconditioning. During this procedure, 90% of the original cystine content is maintained, and 10% extra cystine is created as cysteic acid. No lanthionine is formed[26].

This indicates that less protein is lost while using thioglycolate than when using hydroxides. Both hydroxides and thioglycolate lack carcinogenicity and are not mutagenic. They are regarded as safe if applied correctly and without coming into contact with the scalp[54]. Syed and Naqvi found that the no-lye relaxer (guanidine hydroxide) was less irritating to the scalp than lye relaxer (sodium hydroxide). The authors recommend that African descendants and individuals with very curly hair and sensitive scalp use no-lye relaxers[26].

Thioglycolate and hydroxides are incompatible with one another. The same hair cannot be treated with thioglycolate after hydroxide treatment. Additionally, bleached hair cannot be worn with either. Thus, it is not out of the ordinary to hear from a patient who claims that using a relaxer caused their hair to break or shed. The salon expert must do a test that involves applying the product to a hair strand to demonstrate compatibility in order to prevent errors such as those. The hair is too weak to straighten, or else another relaxer needs to be used if the hair breaks during the test. To reduce hair damage, hair conditioning ingredients can be added to thyoglicolate straighteners[26]. Since 2003, the use of formaldehyde formulations has grown significantly in popularity. Brazil's Rio de Janeiro was the first nation to adopt this technique. Ten years ago, the most popular products were creams or solutions with homemade

formaldehyde formulations created from hydrolized protein, conditioners, and a readily accessible 37% formaldehyde solution that could be purchased over-the-counter and was available in any Brazilian pharmacy. The formaldehyde solution, which is readily available at all pharmacies, was frequently used to sanitize medical equipment and hospitals. The practice quickly gained so much traction that it caught the notice of Brazil's health vigilance groups (ANVISA), which forbade the use of any product that included formaldehyde in quantities greater than 0.2% for makeup and 5% for nail lacquer. Following that, the formaldehyde was swapped out for glutaraldehyde, a neurotoxic and potentially ten times more mutagenic member of the same aldehyde group.

Sterilizers such as glutaraldehyde were easily accessible from hospitals and clinics. Before long, it ceased to be a home-made product and had become a demi-industrialized illegal chemical that was sold in every Brazilian salon. Beautifully colored 500 ml to 1-liter bottles held the solutions. The product was distributed to salons by door-to-door salespeople, and the packaging featured a false ANVISA registration number26. Hair aldehydes' compatibility with all other hair treatment chemicals, such as bleaching, permanent dyes, hair relaxers, lye, and no lye, is perhaps their most intriguing property. In Brazil, chemical relaxers are used to straighten African and Hispanic hair before BKT is applied to improve gloss and smoothness[27].

2.2.7.3.1 Carbocysteine

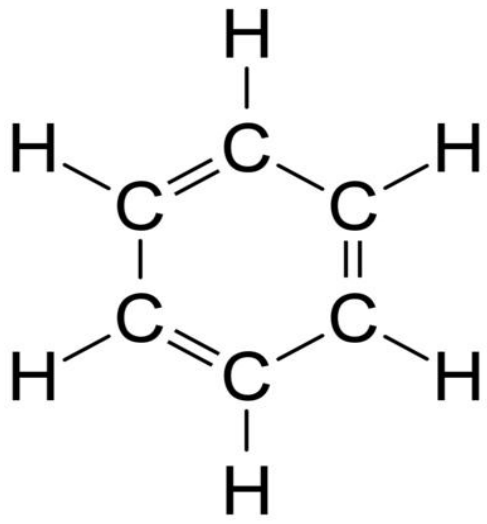
The chemical known as carbocysteine is also known as oxoacetamide carbocysteine or glyoxyloyl carbocysteine. Carbocisteine is a mucolytic substance that has no effect on the keratin in hair that is created by alkylating cysteine with chloroacetic acid. The combination of glyoxylic acid, cisteine, and acetic acid is known as carbocysteine hair treatment. There is an aldehyde functional group in glyoxylic acid. Actually, neither a solution nor a solid form of the aldehyde is

seen. Aldehydes that have substituents that extract electrons generally exist primarily due to their hydration state. Glyoxylic acid reacts like an aldehyde, even though the aldehyde makes up a very small portion of its solutions. As a result, it is regarded as a sensitizer and hazardous material[26]. We may conclude that carbocisteine is not a hair straightening product by itself, and it is formulated combined with an aldehyde such as glyoxylic acid.

2.3 Toxic Chemicals in HCPs

2.3.1 Benzene

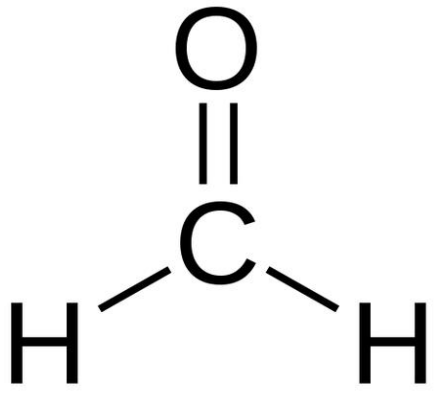
Toluene, or benzene, is a colorless liquid hydrocarbon that is present in petroleum and coal tar. Should that not be sufficient to get you to pause, then maybe this will: The World Health Organization (WHO) states that benzene is extremely dangerous because it is a proven carcinogen that has been connected to problems with reproduction and cancer. It is also known to have an impact on our bone marrow, reducing red blood cell formation. It is a common ingredient in many of our everyday HCPs and is utilized as a solvent in many commercial products to remove grime and oil[28].



Source[15]

2.3.2 Formaldehyde

Preservatives like formaldehyde, which help relax textured hair, are commonly found in natural HCPs. The FDA recently prohibited its use in cosmetics due to its proven carcinogenicity and potential to irritate skin, eyes, and induce hair loss. It has also been connected to asthma in kids and people with weakened immune systems. Thus, formaldehyde in your natural HCPs could be the cause of your sneezing or crying while taking a shower. Other well-known "formaldehyde releasers" are also slipped by manufacturers into their HCPs as a way to avoid FDA regulations. Imidazolidinyl Urea, Diazolidinyl Urea, DMDM Hydantoin, Methylene Glycol, Quaternium-15, and Sodium Hydroxymethylglycinate are some of these chemical components. Formaldehyde is released when they become heated, which is why they are called formaldehyde releasers. There may be more of them out there that we are unaware of[28].

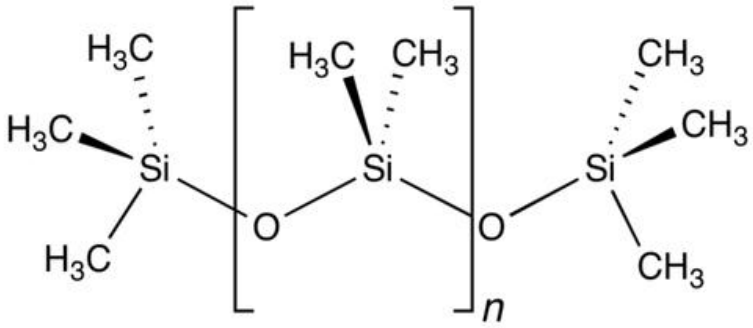


Source[15]

2.3.3 Dimethicone

The greatest HCPs contain the silicone-based chemical dimethicone. Its purpose is to give luster and reduce frizz by smoothing over the hair cuticle. It is so effective at doing this that it irritates the hair and scalp by suffocating them. It accumulates on your scalp since it is difficult to remove

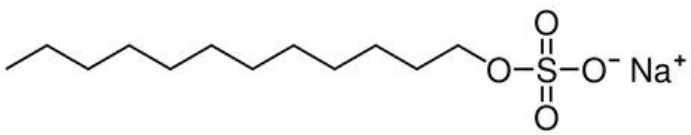
due to its lack of water solubility. It is also a recognized endocrine disruptor that has been connected to uterine cancer and infertility. We promise there are more effective techniques to define and smooth your curls[28].



Source[15]

2.3.4 Sodium Lauryl Sulfate (SLS)

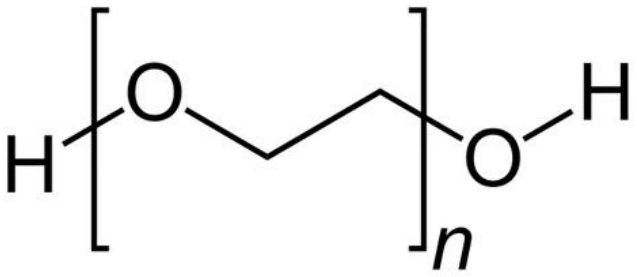
The Skin-Deep Cosmetic Safety Database from EWG rates SLS as "moderately hazardous". "Moderately hazardous" refers to the fact that it has been connected to endocrine disruption, cancer, neurotoxicity, organ toxicity, and irritation of the skin and respiratory tract. It works well to dissolve oil and debris and is commonly used as a foaming component in shampoos and soaps. It's also excellent at depriving your naturally occurring curls of all their dignity, which makes them lose definition and break easily. Avoid SLS and its derivatives for the benefit of the fish, your health, and your gorgeous curls as it is also harmful to asquatic life[28].



Source[15]

2.3.5 Polyethylene Glycol

One of the many synthetic petrochemicals (PEGs) present in natural HCPs and dyes is polyethylene glycol (polyethylene Glycol). PEGs completely deplete your hair and scalp of their natural and protective oils; this particular PEG exposes the skin to bacterial and fungal infections. Additionally, polyethylene Glycol has a high concentration of dioxin, a carcinogenic byproduct of the chemical process that produces it.



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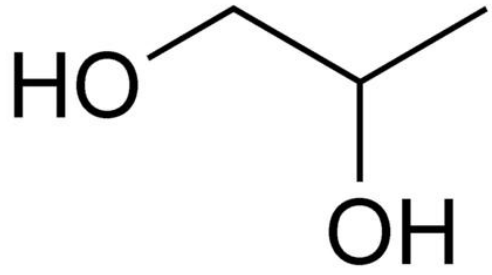
2.3.6 Propylene Glycol

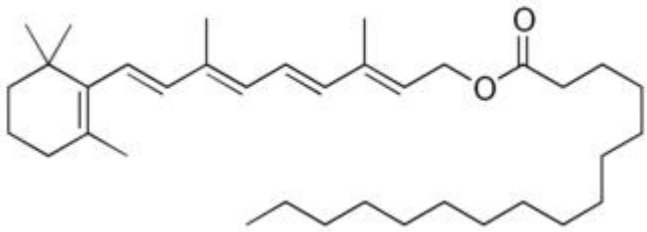
All PEGs have their mother, propylene glycol. Its safety is also hotly contested, mostly since it doesn't bioaccumulate within the body. Although this petrochemical leaves your body within 48 hours of absorption, it still has the potential to do harm while it is in your body. All PEGs have their mother, propylene glycol. Its safety is also hotly contested, mostly since it doesn't bioaccumulate within the body. Although this petrochemical leaves your body within 48 hours of absorption, it still has the potential to do harm while it is in your body[28].



Source[15]

2.3.7 Retinyl Palmitate

Called the prettier relative of retinol, is retinyl palmitate. But it's really not pleasant. It resembles artificial vitamin A on crack. It is applied to textured hair to improve its luster and softness. Additionally, the majority of its source is palm oil, which isn't the most sustainable method of production. Another well-known endocrine disruptor, retinal palmitate is connected to DNA and skin damage from UV radiation, tumor formation, and cell mutation. Additionally, it harms the reproductive system. Thus, stay away from this substance at all costs if you value the Orangatangs and wish to prevent cancer.

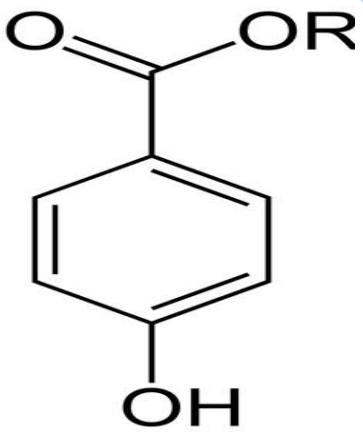


Source[15]

2.3.8 Parabens

A group of similar compounds known as parabens are frequently employed as preservatives in cosmetic goods. To keep the products and customers safe, preservatives can be added to cosmetics to stop the formation of mold and dangerous bacteria. Butyl, propyl, butyl, and ethyl parabens are the parabens most frequently found in cosmetic products. Product ingredient labels usually list multiple parabens, and parabens are frequently combined with additional preservatives to provide enhanced protection against a variety of bacteria.

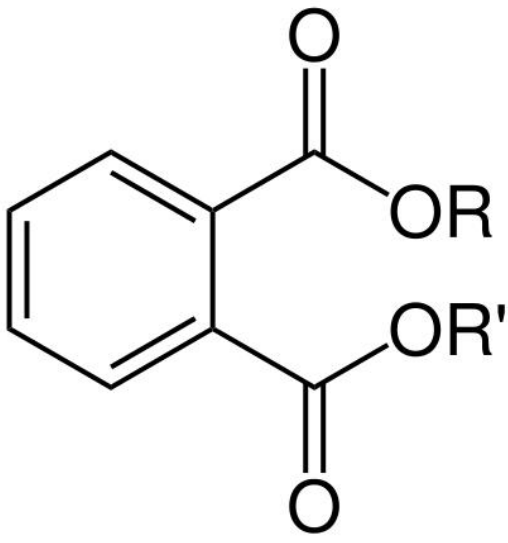
The tiny, crystalline, colorless, odorless compounds are called parabens. At concentrations greater than 0.08%, a pronounced flavor develops. A common description of this flavor is metallic. Therefore, use in food at higher amounts is restricted. On the other hand, parabens are cheap to produce, have no smell, and do not discolor cosmetics. Effective preservatives, parabens function effectively throughout a broad pH range of 4.5 to 7.5. Parabens have high resistance to hydrolysis and stability within the temperature ranges necessary for the manufacturing of cosmetic products.



Source[15]

2.3.9 Phthalates

Phthalates are substances that have the power to soften PVC plastics and harm reproductive systems, particularly in men. That's the reason California outlawed their production of kid's toys in 2009. They are utilized as plasticizers in commercial hair products, like gels and sprays, to give hair more elasticity and hold. Reproductive damage is only one more on the long list of negative side effects. Phthalates have been connected to a number of adverse outcomes, including cancer and preterm delivery. There is also a long list of sly names associated with these that you should learn.



Source[15]

2.3.10 Fragrance

Chemicals equal fragrance. We assure you that even though it is labeled as natural, it is actually a mixture of chemicals that you should avoid using. We would love to talk about the specific compounds that make up "fragrance," but there are countless harmful combinations that may occur. Nonetheless, phthalates are present in them nearly all the time. Anytime you breathe in a

chemical fragrance, your brain is being exposed to harmful vapors. Your reproductive, neurological, and respiratory systems are permanently harmed by this. If the scent isn't specified with the genuine ingredients, such as organic essential oils, you're essentially referring to the deadly frosting on your chemical-laden cake[28].

2.3.11 Sulfates

Sulfates are surface acting agents, or surfactants, that are used to cleanse the scalp of debris and extra sebum. They are employed in your shampoos to create lather. These harmful surfactants include ammonium lauryl sulfate, sodium laureth sulfate, and sodium lauryl sulfate (SLS).

They may even result in frizzy hair and an allergic response on your scalp. Furthermore, if taken for extended periods of time, they may interfere with hormones. Additionally detrimental to aquatic life and the environment are sulfates.

2.3.12 Triclosan

Until recently, triclosan was a significant antimicrobial agent in soap bars. However, it's still present in deodorants, toothpastes, and shampoos. The hormone disruptor is well-known. It is thought that triclosan builds up in fat cells, maintaining a hazardous state in the body.

2.3.13 Colors

We adore when the bottles of shampoo and conditioner have attractive colors. You'll be amazed to learn what kind of substances are used to create HCPs with artificial colors. These hues come from petroleum or coal tar. 'FD&C' or 'D&C' are terms used on the labels to designate synthetic colors.

2.3.14 Resorcinol

Resorcinol, a frequent chemical in bleaching treatments and hair dyes, has been related to skin irritation. In addition, it may result in immune system dysfunction. It interferes with thyroid function in animals.

2.3.15 Selenium Sulfide

One known carcinogen (compound that causes cancer) is selenium sulfide. Selenium sulfide has been linked to the formation of cancers in mice in laboratory testing. Keep selenium sulfide out of your anti-dandruff shampoos by reading their ingredients.

2.3.16 Quaternium-15

Shampoos and conditioners, among other HCPs, include quaternium-15 as a surfactant and preservative. It's a carcinogenic salt made of ammonium. Moreover, it releases formaldehyde. Quaternium-15 may potentially cause irritation to the eyes[28].

2.4 Heavy Metals and their Toxicity Mechanisms

2.4.1 Arsenic

Although the general public believes that all cosmetics are harmless, a number of studies have shown that most of them include heavy metals or other chemicals. Arsenic, a redox inactive metalloid, is a significant environmental contaminant that is present practically everywhere and is known to be a highly poisonous inorganic element. It has the ability to bind to sulfydryl groups in proteins and decrease glutathione[30]. Concerning the greater quantities of As in illegal eye pencils and eye shadows, the appropriate authorities ought to be concerned. The Long-term exposure to As can result in keratosis, hyperpigmentation, vascular problems, and many types of cancer[30]. The study shows that the As concentrations of several of the examined brands are

higher than the maximum recommended level of 2.0 mg-kg set by China. These results confirm that continued As content management in cosmetics needs to be given careful thought[31]. Furthermore, the analysis conducted on five face powders sold in Italy revealed the presence of all the metals under investigation in the range of 0.06-8.0 g/g. Since all of the tested samples (skin bleaching creams) included sizable concentrations of As and mercury, none of them could be deemed suitable for long-term human use[31]. As, an ingredient in pigments used in cosmetics, is currently regulated by the USFDA. Previous research has shown that a variety of cosmetic items, such as lipsticks, eye shadow, lotions, and hair colors, contain As; nevertheless, only the European Union has been found to have stringent laws prohibiting the metal's usage in cosmetics. Under no threshold set by the USFDA or the WHO is As authorized in hair color products[32].

2.4.2 Lead

International restrictions exist for metal contamination in hair coloring products to prevent overexposure to heavy metal ions[33]. One of the primary issues with applying cosmetic products is their high concentration of heavy metals, which is a result of the industrial manufacturing process. People have used cosmetics for thousands of years[33]. Furthermore, a number of studies have examined the potential for dangerous ingredients to be present in makeup and personal hygiene products such hairspray, body wash, mascara, foundation, and skin-whitening lotions.

Based on the findings, electronic debris, paint, and batteries are among the exposure sources in Nigeria. In Mexico, exposure sources include glazed ceramics, polluted utensils, and tainted water; in India, traditional medicines and cosmetics are known to contain lead. Among the exposure sources in France were older homes with lead paint, imported ceramics and cosmetics, and industrial pollution. Concerning substances to stay away from are lead and the common usage of cosmetics[35]. Lead is dangerous for humans and can damage the liver, kidneys, and

nervous system when it comes into contact with these organs. Lead exposure has been connected to hormonal abnormalities, miscarriages, lower fertility in both men and women, and delayed puberty in girls. Lead compounds have been recognized as potential carcinogens to humans[34].

Lead contamination of lipstick can occur by the use of lead-contaminated raw materials or lead-containing pigments. Powders for lead eyes, such as Alkol, Kohl, and Surma, have been connected to mothers and children whose blood lead concentrations are higher[35]. Research indicates that there are notable differences in lead content in lipsticks at different price points[34]. The lipsticks in the Nigerian state of Bayelsa showed the greatest quantities of lead and cadmium, while the lipglosses contained neither of these elements[35]. Lead and cadmium were present in cosmetics such face cream, shampoo, talcum powder, shaving cream, and soap[36]. The research conducted by Ali Zainy in twenty-two lipstick products that were produced locally and imported from the regional marketplace in Jeddah, Saudi Arabia, revealed the presence of heavy metals, including Ni, Cr, Ti, Co, Fe, Mn, Al, Pb, Zn, As, Ba, Cd, etc. Additionally, in a research conducted in Khyber Pakhtunkhwa, Pakistan, samples from every class looked at showed amounts of Pb, Cu, Fe, and Zn higher than the control samples[36].

2.4.3 Mercury

Mercury is a naturally occurring metal element found in the environment. Mercury can occur in numerous forms, but this thick, silver-white liquid is the one that is most commonly associated with it. Many goods, including dental amalgams, electrical switches, thermometers, and various industrial processes, require metalized mercury. In addition to metallic mercury, the element can also be found in compounds composed of other elements. Compounds are the most common type of naturally occurring mercury in the environment. As was already mentioned, the FDA strictly restricts the use of these compounds in cosmetic products[37]. People from all socioeconomic

backgrounds, including the lower and middle classes, have regularly utilized cosmetics as a part of personal hygiene since the dawn of civilization.

Over the past several decades, there has been a considerable increase in the manufacturing of various types of cosmetics, such as creams, beauty soaps, and other items, which are necessary for the maintenance and beautifying of the skin, hair, nails, teeth, and body[36]. Mercury in cosmetics can take two forms: organic and inorganic. Skin-whitening creams and soaps frequently include inorganic mercury, including ammoniated mercury. Among the organic mercury-containing materials in mascara, eye makeup removers, and other cosmetics are thiomersal [ethyl mercury] and phenyl mercuric salts[37]. On the other hand, regular exposure to relatively low levels of mercury may cause long-term neurological and kidney disorders. Mercury in bleaching solutions can accumulate in bodily organs through skin absorption and result in severe poisoning.

Many symptoms and unpleasant reactions, including memory loss, vision issues, irritability, tremors, fatigue, kidney damage, hearing changes, weakness, and even death, can arise from prolonged exposure to mercury compounds[37]. Tests on mercury levels showed that creams made in Asia and the Middle East and purchased from the Saudi Arabian market had T-mercury levels higher than those recommended by the US FDA. Broadly speaking, there is a need to increase public awareness of the dangers associated with mercury exposure as well as the kinds of objects and categories that contain mercury[38].

2.4.4 Cadmium

Cosmetics are becoming a bigger health danger for the general public, despite their beautiful appeal. According to the Food and Drug Administration and the EU's Restriction on Dangerous chemicals, several cosmetic products used by people especially women have been proven to

contain hazardous substances. Given that several of the aforementioned metals are restricted as intended ingredients due to known or suspected hazardous effects, these heavy metals have been connected to a variety of cosmetics to varying degrees[39]. One class of heavy metals that has a density more than 5 g/cm^3 in its natural state is cadmium. All biological species require relatively little amounts of cadmium to survive, but larger concentrations can disrupt metabolism[39]. The dark yellow to orange chemical cadmium is typically found in face powders and lipsticks. Due to its hue, cadmium is utilized in cosmetic items and has been employed as a color pigment in many different industries.

Of all the cosmetic goods examined, bathing soap had the highest levels of lead and cadmium exposure, according to Chauhan's research[40]. Furthermore, even trace levels of heavy metal pollution in cosmetics for beauty have been found to cause skin issues[41]. Check to see if the Kermanshah lipsticks, eye shadows, and hair colors contain cadmium ions. The findings showed that the levels of cadmium in all cosmetic items were much below the limit established by the German organization for food safety and protection (PfS)[42]. The authors call for tighter regulation of cosmetics that are imported both legally and illegally, as well as further research into any potentially hazardous ingredients in cosmetics.

2.4.5 Chromium

Chromium can exist in several valence states, the most common of which is trivalent. The human body, food sources, and dietary supplements all contain the most common type of chromium. Its toxicity is rather low[43]. The cosmetics industry has grown rapidly due to customer demand, especially from women. The everyday usage of cosmetics by people of all ages has become the norm. Several research investigations have demonstrated the potential negative consequences of chromium pollution through several exposure pathways.

These consist of damage to the blood, liver, and kidneys as well as (for instance) lung cancer following inhalation exposure and allergic contact dermatitis following cutaneous exposure after oral consumption[44]. Human skin that is still intact may be able to absorb chromium, and studies have shown that the metal's concentrations are significantly higher in skin that has been wounded than in skin that is healthy. Moreover, chromium is easily absorbed by the skin due to its strong affinity for skin proteins. Sweat accelerates the skin's chromium absorption and has sensitizing properties. When sensitive individuals come into contact with the chromium compound, it might induce contact allergies[48]. Heavy metals were found to be present in detectable amounts in nail polish, foundation, cream, eye liners, lipsticks, mascara, and eye shadows in earlier studies. The eye cosmetics samples had an average of 120.4, 77.3 g kg1 of chromium. The content of chromium was found to be lowest at 1.2 g kg-1 and highest at 197.2 g kg-1[49].

Additionally, according to Lim's research, the blue color category had the highest mean lead and chromium concentrations, measuring 161.8 and 101.6 and 149.4 and 53.1 g kg, respectively. The brilliant shade has a higher chromium 80 content. According to the evidence evaluation, samples of glossy pigment and eye cosmetics, including pearly powder, only contained trace amounts of chromium (VI) (0.3 mg/kg). Chromium (VI) was similarly untraceable in black iron oxide. Three eye shadow samples had levels exceeding 1000 ppm, according to the Corazza study's results, while 28 out of 52 (53.8%) samples had chromium readings over 5 ppm[50].

2.4.6 Nickel

Due to the health risks associated with cosmetic use, the safety assessment of cosmetic goods on inorganic elements has received a lot of attention over the past ten years[51]. Concerns over "toxic metals" and "heavy metals" in cosmetics have been raised by customers. The FDA has examined and tested numerous cosmetic products that are sold commercially for the presence of heavy metals such nickel, chromium, As, cadmium, and cobalt. Soil contains a mineral called nickel. Allergic reactions, skin rashes, and other issues can result from long-term nickel exposure. Furthermore, Group 1 (carcinogenic to humans) and Group 2B (probably carcinogenic to humans) were assigned by the IARC to nickel compounds and metallic nickel, respectively[51].

In the general population, nickel is a significant cause of contact dermatitis due to allergies in both adults and children, with a global incidence of 8.6%. The condition in young females is even more common, at about 17%[51]. There are currently no international regulations for nickel impurity in cosmetics. Based on nickel elicitation experiments, an obstructed dose of 0.44lg nickel/cm^{-2}/week will cause reactions in about 5% of people who are nickel-sensitized. Other than that, skin-penetrating exposure has lower allergy and elicitation thresholds. Only three samples had nickel contents under 5 g/g; the highest values were found in the Italian eye shadow, which had a nickel concentration of 2.76 g/g. The remaining six tests were conducted in China[51]. Furthermore, metallic production tools have the potential to leak heavy metals[52].

Cosmetics frequently include nickel, and some items, including eye shadows and mascara, can exacerbate or even develop allergic contact dermatitis in certain individuals, particularly those with impacted eyelids. Most people with nickel allergy can use commercially available "nickel-free" cosmetics since their nickel content is less than 1ppm. Clinical signs of exposure to nickel include reactions in previously exposed areas (such as flare-up of dermatitis and/or patch test sites), as well as general symptoms (such as fever, headache, arthralgia, malaise) and unexposed

areas (such as pompholyx, flexural eczema, "baboon syndrome," and maculopapular exanthema)[52]. Despite the samples in Concetta Bruzzoniti's study containing a wide range of metal levels (cobalt, nickel, and chromium), the concentrations of bioaccessible elements were either undetectable or very low (less than 0.4 mg/kg)[53]. These samples included pearly powder eye cosmetics. With so many cosmetics on the market, many of which are combined and might have varying exposure patterns and health effects, more research on the safety of cosmetics is required to reduce needless exposure to harmful metals[54].

2.5 Mechanism of PTEs Absorption

Skin dermatoses, which typically shield the subcutaneous layer and internal organs, are a fantastic method for cosmetic substances to enter the body. Cosmetics applied topically eventually find their way into the cell environment via sweat pores, hair follicles, and blood capillaries, fulfilling their intended purpose. Despite the fact that raptness through the skin develops gradually, frequent use of cosmetics over time aids in attentiveness. On the other hand, adding more heavy metal-containing pollutants speeds up the accumulation and also results in toxicity in the form of various illnesses. It seems that there is more harm to the human body when heavy metals are electrophilically substituted with necessary components in vital proteins[55].

2.5.1 Mercury: Melanin Inhibitor Cosmetic Ingredient

Many cosmetic products include mercury, a common but dangerous metal. It usually comes in three varieties: metallic, organic, and inorganic. These types have differing detrimental effects on different body systems, such as the kidneys, skin, lungs, and central nervous system. Mercury is often recognized as a shiny, thick, silver-white liquid that becomes a gas when heated. Mercury is reported to be exceedingly toxic and bioaccumulative. The primary human-caused causes of environmental mercury contamination are said to be mining, incineration, agriculture, and

municipal and industrial waste water discharges[56]. However, it is well recognized that marine life suffers from the bio-magnification of methyl mercury production, which is a primary source of disturbance in aquatic life. Mercury salts are used in cosmetics because they can prevent the production of melanin, which lightens the skin. Many Africans, Asians, Caribbean people, and Europeans with dark complexions often use soaps, creams, and lotions containing mercury to lighten their skin tone[56]. Hg has established a cap of 1 mg/kg (1 ppm) for skin-lightening cosmetics. Many skin-whitening product firms sell Hg levels higher than the permissible limit in order to speed up the whitening process, even though it is illegal in many countries. Eliminating the Hg-containing beauty products section of the cosmetics business will be difficult because it is growing rapidly and is projected to bring in 31.2 billion US dollars by 2024. The most common signs of an excess of mercury include anxiety, joint aches, weakness, tiredness, dizziness, irritability, limb and migraines with evidence of short-term memory loss, acrodynia, and insomnia[57].

2.5.1.1 Mechanism and Hazardous Effect Associated with Hg Absorption

Figure 2.1 depicts a quick, step-by-step change in the Hg following skin application. The blood-brain barrier makes it difficult for inorganic mercury to enter the gastrointestinal tract, central nervous system, or other organs. On the other hand, frequent skin contact can lead to accumulation in the central nervous system, which can result in a range of neurological and behavioral problems. Vomiting, gingivostomatitis, a metallic taste, and excessive salivation are symptoms of intestinal injury. An overabundance of mercury can cause kidney cancer, liver damage, and leukemia, according to the WHO[58].

As was previously mentioned, hg is essential for accelerating the effects of skin-whitening products. It typically stops the body from making melanin. Melanin provides DNA with a natural

defense against ultraviolet (UV) light. Less than 2% of dendritic melanocytes in the epidermis create melanosomes. As melanin is produced in melanosomes, dendrites transport it to nearby keratinocytes. To shield DNA from UV radiation, it settles as supranuclear caps in the perinuclear region of melanocytes and keratinocytes. Beauty products containing Hg-salts considerably suppress the creation of melanin by replacing Cu in the tyrosinase enzyme with Hg-salts. This prevents the development of pigmentation and a suitably dark complexion[59]. When the stratum corneum of the skin is hydrated through intercellular and transcellular channels, mercury is absorbed quite quickly. Once absorbed, it travels to different tissues. Only a little amount of mercury can cross the blood barrier because of its low solubility in lipids. Mercury is especially drawn to the sulfhydryl and thiol groups found in DNA and other molecules.

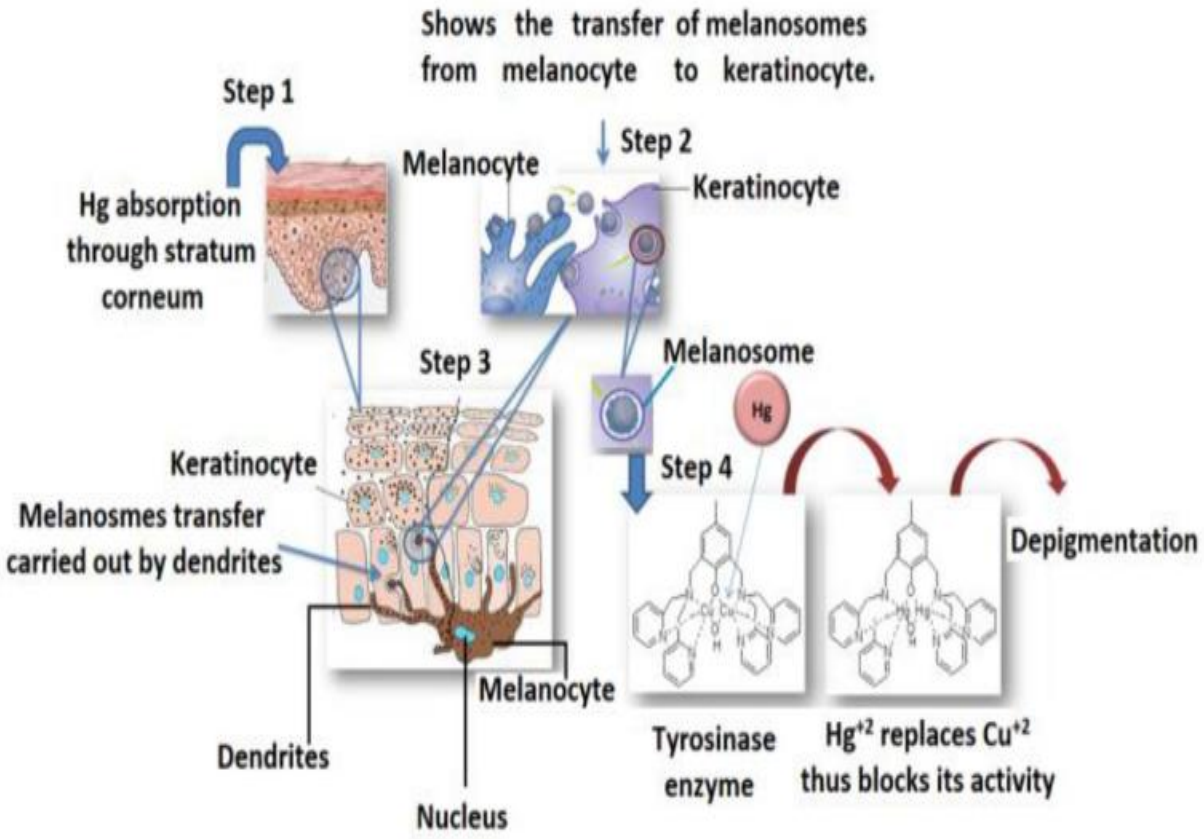


Figure 2.2: The Mechanism of De pigmentation
Source [60]

This changes the macromolecular structure and affects membrane permeability[60]. Therefore, exposure to mercury at the cellular level may cause harm to DNA. Reports state that the mercurous chloride concentration of Mexican face creams was approximately 5.9% by weight, resulting in elevated urine mercury levels of up to 1.88 mg/g creatinine. Chelation therapy using D-penicillamine, succimer (dimercaptosuccinic acid), unithol (2, 3-dimercapto-1-propane sulphonic acid), and meso-DMSA is recommended in this case. In contrast, meso-DMSA and DMPS are superior chelators. The Minamata Convention on Mercury established lower limitations for beauty creams by the FDA at 1 ppm, and the Drug and Cosmetics Act of 1940 prohibited the use of mercury in skin-lightening cosmetics, but these products are still available in other countries[60].

A 1973 US Federal statute also outlawed the use of mercury in cosmetics over the permissible 1 mg/kg level. The European Union has also outlawed the sale of cosmetics containing mercury, such as skin-lightening products, soaps, lotions, creams, and shampoos. Although it is documented, the majority of businesses, particularly those in local industries, employ heavy metal materials without regard for the laws that have been imposed. The most common negative effects of mercury, which accumulates in various bodily sections as a result of consuming cosmetics or other sources that are contaminated with Hg, are as follows[61].

2.5.1.2 Nephrotoxicity

At room temperature, only the poisonous chemical mercury is a liquid. In addition to skin absorption, the respiration and digestive systems of humans can be accessed when using

cosmetics containing mercury additives, which can result in poisoning. Mercury comes in forms that are commonly used in skin-whitening and anti-freckle treatments. These forms include $HgCl_2$, ammoniated mercury (ClH_2HgN), and mercurous oxide (Hg_2O), which usually exhibit hydrophilicity and largely gather in tubules and nephrons and cause chronic tubular necrosis and nephropathy[62]. Nevertheless, nephrotic and neurotic diseases are two notable anomalies connected to mercury intoxication. Numerous studies indicate mercury toxicity from dental fillings, mercury vapor suction, and mercury ingestion in food or medication. The least attention was paid to the most common sources of mercury that must be increased in order to elevate the body's mercury levels. A case report detailing the experiences of a 28-year-old woman using skin whitening products containing mercury was published. Lotion for an extended length of time, nephrotic syndrome was formed. According to the study, there was a progressive increase in the levels of mercury in the urine and blood. Inorganic mercury from the blood enters the kidney's intracellular spaces when a person has proteinuria. There, it binds to proteins that contain thiols, which it then inactivates due to its stronger affinity for. Consequently, this increases the lysosome's susceptibility to Hg^{+2} ions as the primary lysosomes fuse with the cytotic and cytosolic vesicles carrying the Hg^{+2}-bonded sulfhydryl protein[64].

2.5.1.3 Neurotic Syndrome

Another significant disease associated with mercury exposure is the neurotic syndrome, which arises when mercury causes a buildup in the central nervous system. It is believed that proteins and enzymes containing sulfhydryl and selenium are neurotoxic. Mercury attacks the thiol and selenium groups in the neuro-proteins of neuroglia, hence preventing these groups from functioning in intracellular settings and cellular membranes (see graphic abstract). The tubulin protein polymer found in neuronal microtubules, which make up the neuronal cytoskeleton and

have 15 thiol groups in each tubulin monomer, is especially susceptible to mercurial attack[65]. Due to their ability to induce processes such as detoxification of mercury complexation and prevent mercury from being broken down oxidatively into mercuric or mercurial ions by increasing the production of Se-proteins, selenium-containing enzymes serve as a protective agent against neuronal toxicity. However, when the concentration of mercuric ions surpasses that of the complex of selenium-containing enzymes, severe toxicity can cause symptoms like headache, tremors, confusion, migraine, and tremors[65].

2.5.1.4 Tubular Necrosis

The main purpose of the amino acid-based transcellular proteins, which are present in the epithelia and endothelium of every body cell, is to carry various substances, including toxins and drugs, between different body fluids (blood, urine, bile, and intestinal fluids) and organs. Examples of organic anion transporters are Oat1 (a gene linked to a kidney transporter) and Oat (a gene shown to have reduced)[66].

Toxins released by other organs primarily target the kidneys, but the kidneys also filter and remove all toxic compounds from the body's fluids. Once mercuric ions attach themselves to organic anion 1 and 3 and enter the cell, the homeostatic conditions are lost. This is due to competition for the mercuric ions from competing enzymes such as glutathione (GHS), albumin, and metallothionein (MT), which form thermodynamically stable complexes throughout the pH range. The degree of the illness can be ascertained by utilizing Hg^{+2}'s affinity for the Na^{+} and K^{+}-ATPase enzymes, which modifies the Na^{+} gradient necessary for the regular passage of solutes from the extracellular to intracellular environment and stops ATP generation. Cell death, also known as tubular necrosis or nephropathy, is the following stage. Figure 2.3 details the precise mechanism of Hg absorption and cell death[67].

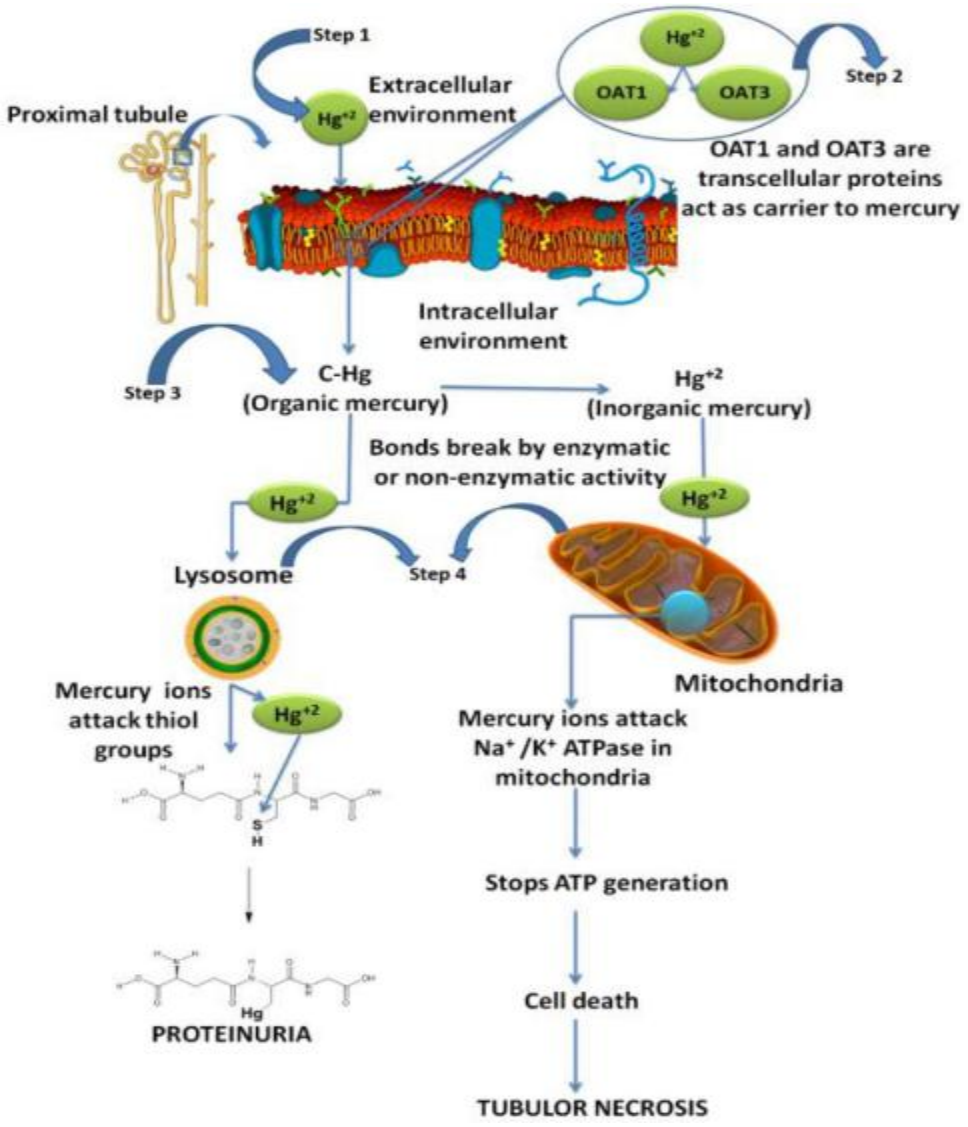


Figure 2.3: The Basic Principles of Nephrotoxicity
Source[67]

2.6 Lead: Color Additive in Cosmetics

The color colors of the products are often the primary forces behind the growth of the cosmetics sector. Different color additives are used to create a wide spectrum of color tones. However, using color additives incorrectly leads to tainted cosmetics, and selling such products is forbidden. Therefore, before they may be used in cosmetics, FDA approval is needed. The FDA's "listing regulation" covers the approved color additive and details the maximum allowable impurity level as well as the reasons for granting clearance[68]. Lead is a soft, malleable heavy metal with an atomic number of 82. When compared to most common metals, it is denser. Because of its ionization energy (715.6 kJ/mol), which is similar to many metals that create color, such Ni, Mg, and Mg, it is an excellent option to utilize as a color additive in medications, food, cosmetics, and numerous medical devices.

Since ten million tons of lead are produced worldwide each year on average, lead is inexpensive. The USFDA normally limits the amount of lead used in cosmetics as color additives to between 10 and 20 parts per million. Lead is frequently added to lipstick, other lip cosmetics, eyeliners (kohl, kajal, al-kahal, surma, tiro, tozali, or kwalli), and cosmetics that are used externally. In the Middle East, eyeliner that has more than 50% lead is applied using kohl, a kind of traditional material. According to published research, the mother of a seven-month-old infant breastfed him and frequently used eyeliner while she was pregnant, which resulted in 39 g/dL of lead in his blood[69]. Pb is detected in lip cosmetics, such as lipstick and lip gloss, below the 7 ppm ICP detection limit, according to data from FDA-funded research. Nevertheless, Pb levels were 14 ppm below the detection limit when hundreds of additional externally applied cosmetics, including body lotions, blush, shampoo, eye shadow, and blush, were examined by ICP[69]. Lead was also added to hair colors as lead acetate to provide a gradual coloring effect. Lead acetate

was approved as a color additive in 1980. However, on October 30, 2018, the FDA forbade the use of lead acetate in hair dyes as part of the amended "color additive regulations" laws. Lead stays in the environment because of its reactivity and lack of biodegradability. Antioxidant molecules such as glutathione peroxidase, superoxide dismutase, glucose 6-phosphate dehydrogenase, heme-producing enzymes, and thiol-containing antioxidants are the main targets of lead poisoning. Low blood lead levels can reduce the activity of many of these enzymes as well as the effects of those that worsen oxidative stress by increasing the generation of reactive oxygen species (ROS). A significant Pb buildup is not necessary to completely limit the action of any type of enzyme. Lead toxicity primarily results from oxidative stress pathogenesis[70].

Although Pb poisoning also affects the body through a variety of other cellular, intracellular, and molecular mechanisms, its main target is the central nervous system. Among these techniques include oxidative stress induction, rapid neuronal cell death, and disruption of Ca ($^{2+}$)-dependent enzymes such as nitric oxide synthase. The onset of autoimmunity, a condition in which an individual's immune system attacks its own cells, learning disabilities and mental retardation, intrauterine fatalities, and hearing impairments are among the more severe symptoms of lead poisoning[71]. Moreover, published population studies establish a direct link between Pb exposure and the development of hypertension and cardiovascular illness in the future. It is believed that the primary target for Pb-induced toxicity is the vascular endothelium. The next section discusses the mechanisms that underlie the toxicity of lead in the primary Pb targets[71].

2.6.1 Oxidative Stress Induced Disorders

Oxidative stress is known to be the cause of chronic human disorders. Raised blood levels of lead (Pb-BL) induce the creation of reactive oxygen species ($H2O^{+}$) such as superoxide anion, hydroxyl radical, and hydrogen peroxide, and reactive nitrogen species (Nitric oxide). Quenching

the cellular antioxidant pool is the second step. The suppression of -aminolevulinic acid dehydratase (ALAD), which is caused by an increase in Pb-BL, is the primary cause of ROS and RNS. ALAD is a heme biosynthetic enzyme[72]. As a result, -aminolevulinic acid (ALA) accumulates and accelerates the generation of reactive oxygen species. Pb-induced damage is also encouraged by factors that affect the antioxidant cellular defense system (ACDS)[72].

Enzymes such as glutathione peroxidase (GPx), catalase, glucose-6-phosphate dehydrogenase (G6PD), and superoxide dismutase (SOD) work in tandem with ACDS to protect the organism against reactive oxygen species (ROS). Pb has a promising affinity for the thiol (-SH) group that all of these enzymes possess. Elevated Pb-BL significantly inhibits the activity of these enzymes. Owing to its divalent nature, it has detrimental consequences when it replaces several essential divalent elements, such as Zn, Se, Mg, etc., from numerous biomolecules. Moreover, it aids in the decrease of glutathione (GSH), a tripeptide component of antioxidant defense that is not enzymatic[73].

2.6.2 Renal Diseases

Pb is a well-known toxin that damages the kidneys, particularly the renal cortex. Renal tubular necrosis is caused by an increase in Pb-BL. Glycosuria, aminoaciduria, and phosphaturia produce acute lead toxicity in the proximal tubule. About 90% of the albumin protein found in erhrocytes is bound by Pb. It was also associated with renal tissue and oxidative cell damage. $Pb(^{+2})$ competes with $Ca(^{+2})$, disrupting $Ca(^{+2})$'s homeostasis. As a result, the mitochondria release $Ca(^{+2})$, which damages the mitochondria by causing mitochondrial enlargement and cell death through apoptosis, both of which change how lipids are metabolized. It also initiates the opening of the mitochondrial permeability transitional hole[74].

Furthermore, Pb-exposed HEK293 kidney cells show reduced lipid peroxidation, lipid distortion, cell survival, loss of cohesiveness, and production of superoxide anion. Apoptosis in the proximal tubules is most likely the source of Pb-induced cellular damage. Research on the proximal tubules of rats revealed that it decreases endoplasmic reticulum while increasing the systolic concentration of calcium in the mitochondria[73,74].

2.6.3 Alpha Thalassemia: Mental Retardation

Many studies have been published on the relationship between Pb-BL and Alpha thalassemia. Women are especially susceptible to lead exposure due to the regular use of cosmetics containing lead (Pb), which has been demonstrated to be a silent toxin. Lead exposure, even at low levels (0.01 mg/g), can be detrimental to the brain. Mice exposed to Pb for 30 days developed Pb-induced structural lesions that were apparent under a light microscope, per histopathology data[75]. When young animals are exposed to lead, their brains' cytochrome concentrations may somewhat increase as a result of either a more general reduction of brain growth (such as preventing protein synthesis) or a specific suppression of heme-synthesis[75]. Mental impairment is brought on by epigenetic alterations brought on by a mutation in the chromatin regulator gene ATRX X-linked syndrome (ATR-X). This syndrome presents with hematological anomalies, a distinct facial gestalt, mild to severe impairments, and infantile expressive language dysfunction[74]. Figure 2.4 illustrates Pb's method of action in outline form[75].

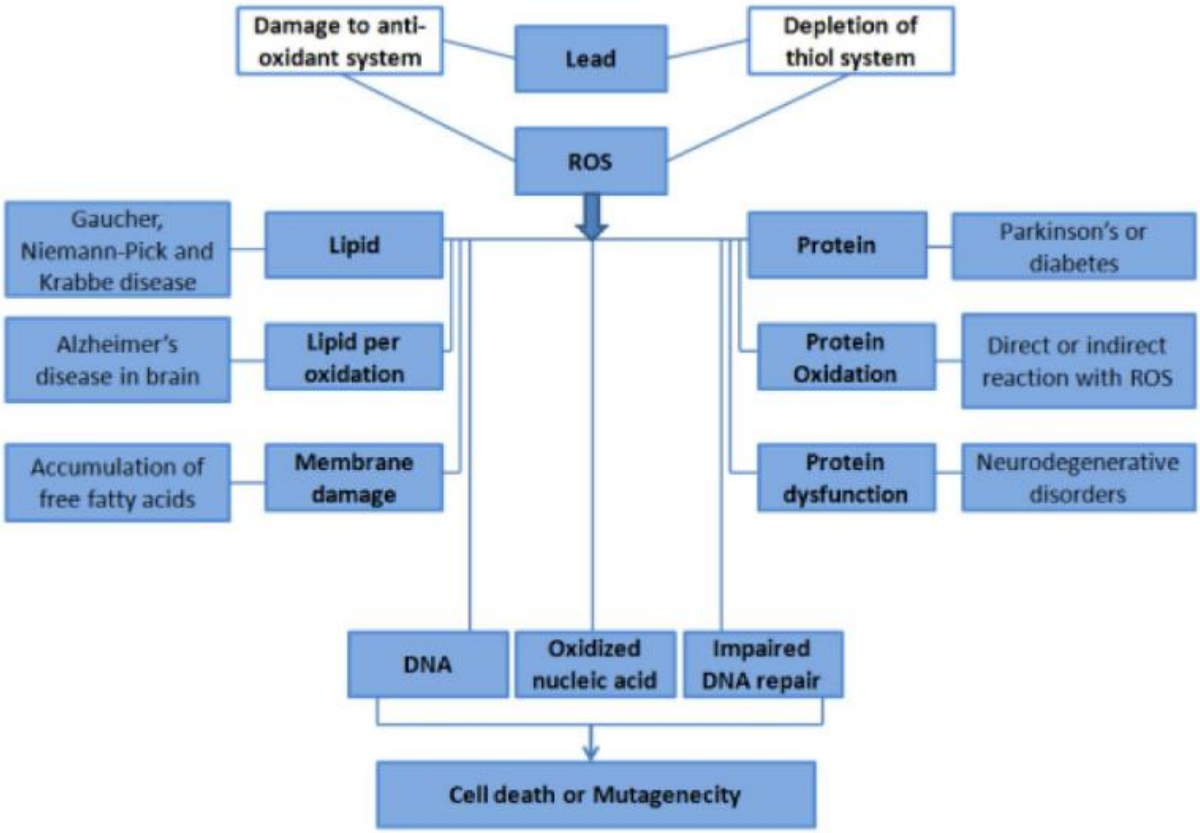


Figure 2.4: Oxidative Stress Caused by Lead
Source[75]

An analysis of a study indicates that high levels of Pb exposure in nursing rat pups enhances ADP-independent respiration in the brain and mitochondria while postponing the establishment of brain dicarboxylic amino acid metabolism. Furthermore, epidemiological research has found a link between slightly higher Pb exposure and mental impairment.

2.6.4 Placental Exposure

Once the heavy metal lead crosses the placenta and blood barriers, it keeps building up in the tissues of the developing fetus. Because the blood barrier is still forming and the fetus is vulnerable to neurological issues, it has been noted that the use of cosmetics containing lead may have an effect on developing fetuses[76]. Lead poisoning is primarily caused by lead substituting calcium in the nervous system, which impacts hippocampal-mediated learning and memory activities. Lead harms the reproductive organs by either directly or indirectly interacting with hormones through the hypothalamic-pituitary glandular axis.

Epidemiological research indicates that low birth weight (LBW), spontaneous miscarriage, minor abnormalities, and preterm delivery are among the poor birth outcomes associated with maternal or paternal lead exposure[77]. The odds ratio (OR) of 1.96 indicated a substantial increase in the likelihood of preterm deliveries after adjusting for variables; this association was more pronounced in mothers aged 25 to 36, with an OR of 2.03[77].

An accumulation of lead in tissues or organs triggers a variety of mechanisms that cause necrosis and apoptosis, which kill off neuronal cells[78]. The Na+/K+ ATP in the cell membrane is blocked, which affects energy metabolism and the release of calcium from mitochondria. Additionally, it results in the production of reactive oxygen species, which initiate the cascade of apoptosis. Cellular disintegration can be caused by chromatin condenses, mitochondrial malfunction, nuclear shrinkage, DNA breakage, and membrane blebbing. An increase in apoptosis during fetal development may be the cause of children's learning and memory issues[78]. Additionally, it enters the CNS and impairs embryonic growth by interfering with normal cell functioning and leading to aberrant skeletal growths[79]. Additionally, it inhibits the thyroid stimulating hormone's function, which reduces the growth of soft tissues, lowers birth weight, and impairs the delivery of nutrients to the fetus, as illustrated in Figure 2.4. infant epigenetic It is theorized, based on studies completed at 12 weeks'

gestation, that prenatal Pb exposure changes the DNA methylation of imprinted genes, resulting in rapid development and low birth weight. Pb in the peripheral blood of 321 women was analyzed using inductively coupled plasma mass spectrometry (ICP-MS). Additionally, children and adolescents that are exposed to pb have lower cognitive performance[80].

2.6.5 Cadmium: Color Pigment in Cosmetics

Cadmium, an atomic number 48 soft silvery-white metal, was discovered for the first time in 1817. There is an average of 0.1 to 0.5 ppm in the Earth's crust. It is processed and utilized in many different industrial applications, including as paints, batteries, pigments, plastic stabilizers, coatings for solar panels, fuel rods for fission reactors, and many more. The FDA classified it as a dangerous metal that can result in severe intoxications in the late 20th century. Japan has documented cases of itai-itai illness, a severe intoxication caused by Cd. Color pigments are the most well-known application for cadmium; cd-compounds are commonly found in pigments that are yellow, orange, and red in color[81].

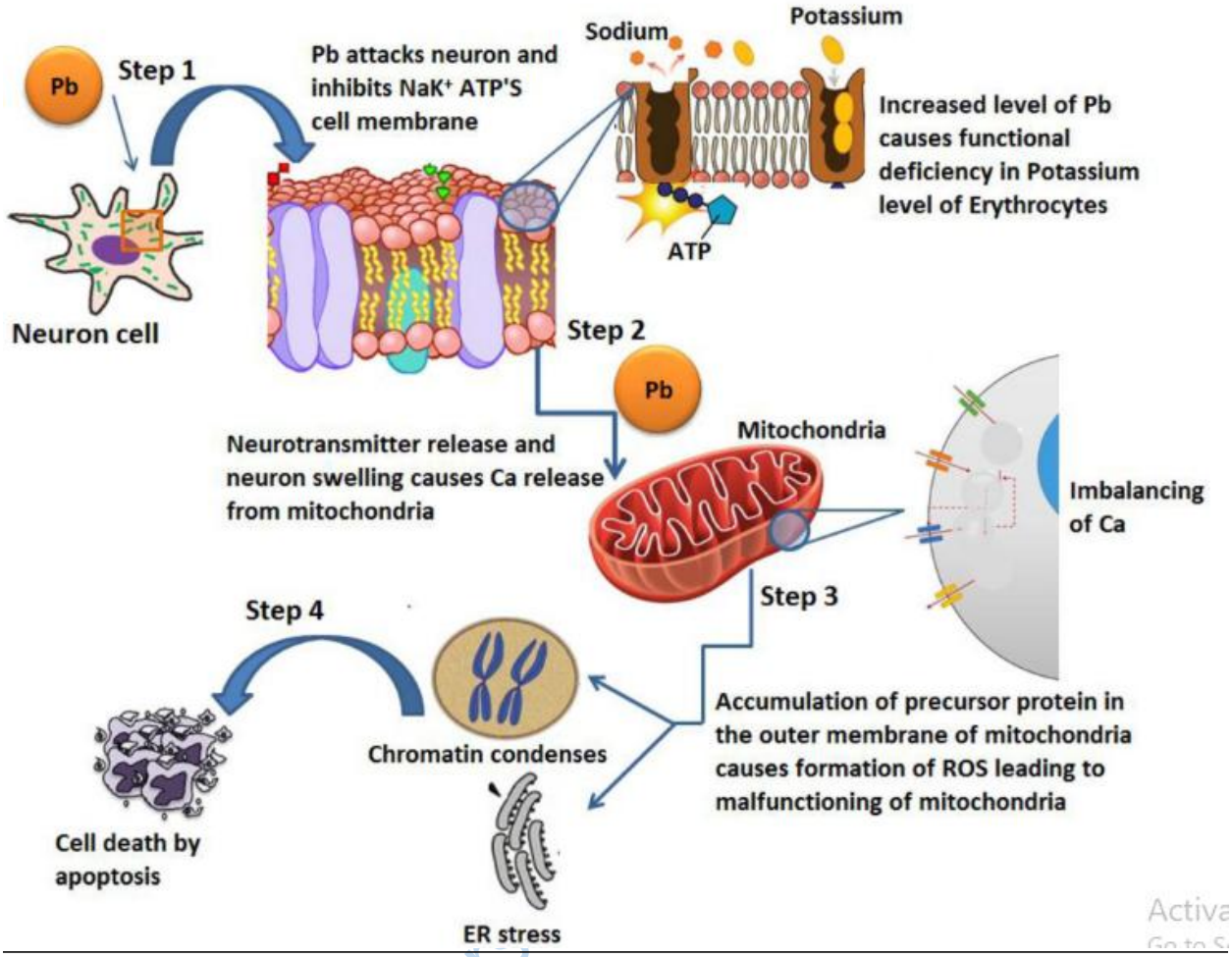


Figure 2.5: Mechanism of Fetal Lead Poisoning.
Source[82]

Cadmium sulfide can be used by anyone who wants a yellow tint; selenium doping enhances the tone to black. It was also used with chromium oxide to produce a pale green tone. As a result, all cosmetics that are applied topically to alter skin tone include cadmium. However, safety precautions are taken to ensure that the amount of CD used stays below the FDA-specified limit. These are incorporated into externally applied cosmetics to produce various hue tones. As a result, these firms must adhere to good manufacturing practices (GMPs). One of the most serious side effects of this hazardous metal, which is present in eye liners, lip gloss, lip pencils, and beauty items, is severe proteinuria[82]. There are two possible ways to help the skin absorb Cd when makeup is applied to the face: either attaching free Cd-ions to cysteine sulfhydryl radicals in epidermal keratins or activating and complexing with metallothionein.

The Cd is then discharged into the blood pool, where it attaches itself to erythrocyte membranes, blood albumin, or MTs to travel throughout the body. When exposed briefly, it primarily builds up in the liver; however, when exposed repeatedly, it attaches to tiny proteins and travels to the kidneys, where it is filtered in the glomerular tubules and reabsorbed into the proximal tubular cell. As a result, the kidney buildup progressively causes severe symptoms[82]. Regular users of cosmetics containing CD run the risk of passing the chemical on to their fetus through breast milk or during pregnancy. The buildup of cadmium in placental tissues can hinder nutrition delivery and the production of steroid hormones. Bathing soaps with 0.03 ppm to 0.04 ppm of Cd have been linked to an increased risk of kidney, prostate, lung, and pancreatic cancers. Cadmium has a No Observed Adverse Effect Level (NOAEL) of 0.005 mg/kg. Consequently, the following sections address the issues brought on by exposure to CD[83].

2.6.6 Kidney Dysfunction

Following absorption, the blood's greatest concentration of Cd is found in the liver and kidney. Therefore, long-term kidney damage may ensue from environmental or cosmetic product-related Cd exposure. In southern Sweden, 820 women (71% participation rate) between the ages of 53 and 6492 participated in the Women's Health in the Lund Area (WHILA) population-based women's health survey. The results showed that cadmium exposure was significantly associated with renal tubule disorder when levels of exposure reached 0.38 g/L in blood and 0.52 g/L in urine. Furthermore, it has been found that women frequently have higher levels of CD than men do[84]. Because there is no excretory system in place, only a very tiny amount of Cd that has accumulated in the kidney is released into the urine.

Furthermore, free filtered cadmium in the renal proximal tubule and Cd's preferential absorption by receptor-mediated endocytosis of Cd-bound metallothionein (Cd-MT) cause Cd to accumulate in the kidney. The body's lysosomes and endosomes break down internalized Cd-MT, releasing free Cd into the cytosol where it triggers cell death pathways and produces reactive oxygen species (ROS). Renal failure brought on by prolonged cadmium exposure leads to the clinical manifestation of Fanconi syndrome[85]. There are three main thresholds for the concentration of Cd in urine, the first of which produces biochemical changes at about 2 mg/g creatinine. The second results in cytotoxic symptoms, high-molecular-weight proteinuria, and a creatinine level of roughly 4 mg/g. Concentrated albumin in the urine is frequently an indication of glomerular failure. Damage to the renal tubules caused by chemicals has been linked to an increase in the excretion of N-acetyl-b-d-glucosaminidase (NAG) and alanine aminopeptidase (AAP) in the urine. The third threshold is associated with tubular proteinuria, which is caused by around 10 mg/g of creatinine and a decreased tubules' capacity to reabsorb low-molecular-weight proteins[86].

2.6.7 Osteosporosis

Low bone mass and skeletal microarchitecture degradation, which lead to fragility and a higher risk of fractures, are characteristics of osteoporosis[87]. The late 1940s saw the discovery of the first cases of osteomalacia and renal decline caused by Cd poisoning in Japan. Itai-Itai sickness, the most severe type of Cd-intoxication, has been linked to kidney and bone damage[90]. Patients with Itai-Itai sickness had urine cadmium levels ranging from 20 to 30 g/g creatinine. Comprehensive epidemiological investigations conducted recently have shown that there is a positive correlation between increased cadmium exposure and the substitution of calcium by cadmium[87]. This results in a decrease in bone mineral density and an increase in the frequency of human fractures at lower exposure levels. Cadmium acts directly on bone cells in a bone culture system at low concentrations to promote bone resorption and prevent bone formation without influencing the hormone levels in the blood, gut, or kidney.

The effects of mercury poisoning on the mineral content of the lumbar spine and femur bone were tested in a male rat model[87]. Using dual-energy X-ray absorptiometry (DEXA), the amount of bone damage in these male rats was determined[87]. Severe calcium excretion from the kidneys is indicative of tubular failure and bone mineral loss. It can also reduce the kidney's ability to create active vitamin D, which means that there will be less of it and that the duodenum and distal convoluted tubule will take longer to actively reabsorb calcium. This is the main cause of osteomalacia and osteoporosis, particularly in the elderly. However, cadmium may also directly affect bone turnover by lowering the quantity of collagen produced and the bone's ability to mineralize[87]. Cadmium (Cd) has three main effects on bone: first, it interferes with the normal activation process of renal tubular damage, which is then followed by vitamin D; second, it interferes with calcium; the exact mechanism behind cadmium-induced osteoporosis is still

unknown; third, it directly affects bone density; and finally, it directly influences bone metabolism without endangering the kidneys[88].

2.6.8 Chromium

Chromium metal, which has an atomic number of 24, is a brittle, shiny, steely gray material. It serves as an essential anti-corrosive agent in stainless steel. Though it was thought to be the necessary component, the European Food Safety Authority (EFSA) decided in 2014 that there wasn't enough data to categorize Cr as necessary. The most prevalent allergen is present in foundations, lip cosmetics, eye makeup, soaps, and other items where it acts as a colorant[89]. Its color level varies from 0.50 to 2.70 parts per million, but its valence state determines how harmful it is. While hexavalent Cr (Cr(VI)) is not found in nature and poses health risks to humans, including being poisonous, genotoxic, and carcinogenic, trivalent Cr (Cr(III)) is recognized as an essential element required for proper energy metabolism[89].

The mechanism is commonly associated with cellular reduction processes that produce ROS and Cr metabolites, which have a range of genotoxic consequences, such as changes in somatic cells that induce the growth of tumors. The mechanism behind chromium carcinogenicity is essentially the result of exposure to hexavalent chromium to cancer stem cells. Skin can absorb hexavalent chromium more readily when it is washed. Nevertheless, both forms of chromium also function as haptens in the development of contact allergies[83]. Its activity is often mediated by the cell converting Cr(VI) to Cr(III), which reacts with the proteins and DNA of the cell to produce ROS. Furthermore, adducts between DNA and chromium (III) cause mutations[81,88]. Cosmetics use a lot of hydrated chromium and chromium oxides, especially in soaps. Many studies were carried out to find out how much Cr was present in different cosmetics, how often customers were exposed to it, and how it affected their health. Based on statistical analysis, the

skin on the face exposed to a cosmetic product containing Cr between 0.1 and 3.2 g/g was exposed to between 0.0002 and 0.003 g/Cm2, which is significantly less than Cr(VI), which was 1 g/Cm^2. It can cause severe skin ulcers and swelling, breathing problems (asthma), running noses, intense redness, coughing, shortness of breath, wheezing, nasal lining irritation, and nose ulcers if inhaled in high quantities[86]. Cr can cause allergic contact dermatitis and cause major injury to the kidneys, liver, circulatory system, and nervous system when it accumulates in the corneal layer. It was recently reported that cosmetics and makeup contain trace amounts of chromium.

The NOEL (No Observed Effect Level) value for humans is provided in this study along with information on the many metals that are present in these items. At this concentration, Cr cannot provide a significant health danger to persons; nevertheless, if used regularly, it can have a deleterious effect on human health or even cause the onset of cancer when paired with environmental risk factors[88]. Most eye shadows available for purchase in almost every country have a higher concentration of Cr. The maximum quantity of Cr present in toy cosmetic kits' eye shadow was 3620 g/g, but the range of Cr concentrations in beauty kits sold in Egypt was 16.05 to 29,800 g/g[88]. The minimal risk factor associated with chromium is covered in the section that follows.

2.6.9 Cr-Induced Toxicity

In cosmetics intended for external use, chromium oxide and chromium hydroxide greens can both be utilized as colorants. Since Cr has the least hazardous profile of any substance and is even more useful as a color pigment, the FDA has not enacted restrictions restricting its usage in cosmetics. The most common and harmful adverse effect of Cr that people report having is skin allergies. Multiple studies have reported that the Cr(VI) minimal eliciting threshold (MET)

varies between 1770 and 9 g/g. 36% of patients responded to a Cr(III) at or below 8850 g/g, whereas 64% did so at or above 17700 g/g, according to a different study by the same investigator[89]. Mercury, chromium, cadmium, and lead carcinogenic risk factors were computed in a relatively recent study, although no relevant toxicity data was available at the time of publishing. In a cosmetic cream sample, the incidence of cancer related to chromium was determined to be 1.32. As per the specified restrictions, a carcinogenic (causes cancer) risk of 10^{-6} to 10^{-4} is considered acceptable. Applying chromium in external cosmetics does not increase the risk of cancer, as the anticipated value is far lower than the permitted cancer risk value[88].

2.7 Hair Toxic Metals Levels in Relation to Environmental Exposure, Diet and Lifestyle

Hair has been utilized in numerous studies in the past to determine the likelihood of exposure to high quantities of hazardous or potentially hazardous substances through food or water. While certain metals, like copper, seem to have a relatively low affinity, others have a tendency to collect in the hair. After examining more than 400 studies on the use of hair for toxic metal detection, the US Environmental Protection Agency (USEPA) came to the following conclusion: "Hair is a meaningful and representative tissue for biological monitoring of exposure to antimony, nickel, lead, chromium, copper, As, mercury, cadmium, vanadium, and possibly tin and selenium[90].

Numerous population studies under USEPA supervision have shown that hair trace element concentrations may be an indicator of exposure in poisoning and deficiency situations. Within a single metropolitan region, correlations were discovered between hair values and environmental exposure to barium, chromium, lead, mercury, nickel, tin, and vanadium levels. The statistical analysis took into account factors including smoking behaviors, age, sex, and hair color. In the hair specimens, a number of metals exhibited a propensity to increase and decrease together,

which was consistent with results observed for other human tissues[90]. The study's findings indicated that the concentrations of trace elements in hair and other tissues correlated positively. The authors clarified that exposure connections should not be confounded with metabolic status, which is a distinct and complicated issue[88]. Childhood lead poisoning is a global concern due to the high sensitivity of lead exposure, especially in industrialized countries113. Researchers examined the blood and hair of 189 youngsters to determine the level of environmental lead exposure that the children in one of Russia's contaminated areas were exposed to. Establishing hair lead value which may be regarded as a "level of concern" was another aim of the study. The study's findings showed that, only in samples taken close to battery factories, there was a strong correlation between the amounts of lead in dust and soil and the levels of lead in hair and blood. However, a significant link between hair lead levels and ambient lead was not established after excluding that group of samples[90].

The majority of people are exposed to mercury in various chemical forms. The two most significant ways that people might be exposed to mercury are through eating seafood and dental amalgam fillings that release mercury vapor. Total and inorganic mercury were measured in whole blood, red blood cells, plasma, urine, and hair samples in a study including 28 people[91]. The authors found that the greatest indicator of long-term average exposure to methyl mercury appears to be the total concentration of mercury in hair, as there was a strong correlation between total hair and total blood mercury. Kim failed to establish a linear link between exposure to mercury from fish and other sources, including amalgam or occupational exposures, when conducting a cross-sectional study in Korea to measure mercury amounts in the hair of mothers and children at high risk of mercury exposure[92]. Mercury levels did, however, positively linked

with motherhood[70]. According to Stupar's findings, hair can be used to estimate corresponding air concentrations and, in some situations, to quantify exogenous atmospheric exposure[92].

Valentine examined samples of blood, hair, urine, and tap water from people who were exposed to different levels of selenium through their home well water. While blood selenium and well-water selenium did not significantly correlate, concentrations of selenium in urine and hair showed strong positive associations with selenium levels[93]. The results showed a substantial association between urine selenium and blood selenium as well as between urine and hair selenium. There was no discernible relationship between blood and hair selenium.

Manganese (Mn) is known to have neurotoxic effects when exposed to high ambient concentrations. In the pilot trial, children exposed to high levels of Mn in their drinking water displayed hyperactive behavior in accordance to their Mn hair level. The group that drank the water with the higher Mn concentration demonstrated a significantly higher score at the Hyperactivity T-score[93]. In a related study, the levels of As, manganese, and cadmium were examined in hair samples taken from thirty-two students. As and Mn hair concentrations have been found to significantly inversely correlate with children's cognitive function[93].

2.7.1 Techniques for Evaluating PTEs in HDPs

2.7.2 Atomic Absorption Spectrometry

In order to determine the chemical composition of HDPs, atomic absorption spectrometry (AAS)-based methods have been utilized extensively[94]. It is commonly used to determine elements at mg L-1 levels using flame atomic absorption spectrometry (F AAS) and at g L-1 levels using graphite furnace atomic absorption spectrometry (GF AAS) for this purpose." GF AAS direct analysis has been carried out, and these protocols have been adjusted for flow injection systems[94].

Flame atomic absorption spectrometry is the most widely used technique for determining the chemical components of cosmetics[30,94]. To create solutions that are compatible with F AAS analysis, meticulous sample preparation is necessary because samples are normally delivered into the apparatus using a standard nebulization technique[17,94]. The flame that is typically utilized in cosmetics analysis is composed of air, acetylene, and a sizable quantity of an oxidant related to acetylene. F AAS has a lot of disadvantages despite its dependability and reasonably priced equipment, including as low throughput due to its single element analysis capability and comparatively low sensitivity in comparison to other spectrometric methods (ICP-OES and ICP-MS). Moreover, both spectral and nonspectral interferences may introduce uncertainty into the outcomes of the F AAS research. Ionization effects, transfer to the atomizer, background nonspecific absorption, and atomic line overlap are the main causes of interference in F AAS. But the majority of these interferences are well-known and manageable[94].

Cr, Ni, Cd, Pb, Cu, and Zn are the elements that are most commonly found in cosmetics, according to F AAS. Cosmetics were also found to contain low-frequency elements K, Na, and Bi as well as F AAS, in addition to other elements like Co, Mn, and Fe. Additionally, the F AAS has been used in conjunction with cold vapor generation (CVG) and hydride generation (HG) systems to assess the amounts of As and Hg in cosmetics, respectively[30,94]. The target species is converted into a volatile hydride in the HG-AAS104 and fed into an atomizer. In acidic conditions, reducing agents most commonly $SnCl_2$ or $NaBH_4$ produce atomic vapor. Conversely, the CVG-AAS method involves the reduction and direct volatilization of mercury as free atoms, with the absorption occurring in an unheated quartz tube. Because they reduce matrix interferences during the analyte's extraction from the matrix, these methods have been used for cosmetic analysis. The enhanced capacity of the quartz cell to transfer analyte vapors results in

better LODs[94]. The hydrides may be diluted in the gas phase, result in moist vapor during atomization, or encounter matrix-related interferences or concomitants at high concentrations (such as transition metals) that inhibit the production of vapor. To avoid overly optimistic or pessimistic outcomes, these interferences must be thoroughly investigated. Atomic absorption spectroscopy in a graphite furnace has also been used to analyze the chemical components of cosmetics. Cosmetics feature a complex matrix due to the different concentrations of organic and inorganic ingredients. Thus, in order to provide increased sensitivity and minimize potential matrix-related interferences, it is possible to highlight the ability to complete an adequate heating program as one of the essential features of GF AAS. Since graphite furnace atomic absorption spectroscopy is one of the most sensitive methods and has a great knowledge of complex matrices, it is a wise choice[30]. Most sample matrix interferences can be removed by combining an appropriate chemical modification to increase analyte thermal stability with an effective background corrector, such as one based on the Zeeman effect.

Although the GF AAS approach can be used for cosmetic analysis, care needs to be taken to ensure that analytes do not lose their integrity during pyrolysis because even at low temperatures, they can volatilize. It is best to utilize an appropriate chemical modifier to slow down this process. In cosmetics analysis, different chemical modifiers, such as NH_4H_2, $PO_4Rh(NO_3)_2$, $Pd(NO_3)_2$, and $Mg(NO_3)_2$, have been used to increase matrix volatility or analyte thermal stability. Several temperature programs have been employed in accordance with the analytes and matrix, and calibration curves in the sample medium have also been proposed as a means of simulating sample behavior. However, GF AAS does have certain limitations. One such limitation is the use of a lower sample volume, which may lead to results with a high standard deviation because of a lack of homogeneity. The method's monoelemental capacity necessitates a

thorough analysis and meticulous assessment of several factors, including atomization and pyrolysis temperatures, the use of chemical modifiers, and the mass of each sample and element. Pb is the chemical element most commonly detected in cosmetics, according to GF AAS. Using GF AAS, low frequency As, Cu, and Cd, other elements like Co, Ni, and Cr have also been found in cosmetics. GF AAS allows for fast sample analysis, yet the majority of research published in the literature evaluate cosmetics after the sample has been digested[93,94].

2.7.3 Plasma-based Techniques

ICP-OES and ICP-MS spectrometric techniques are used to identify potentially hazardous and toxic ingredients in cosmetics. Numerous studies and publications on these two methods may be found in the literature. However, in order to prevent nebulization system clogging, carbon deposition on the equipment's interface, and other often seen interferences, using an effective digesting method is necessary to produce digests with low carbon content and little to no suspended solids[17,30,94]. Due to their multielement capacity, low limits of detection and wide linear range, the ICP-OES and ICP-MS techniques are selected for element identification in various matrices.109,111.

Despite these benefits, a range of spectral and non-spectral interferences can affect the results of ICP-MS and ICP-OES. The physical characteristics of the digests made by sample preparation techniques are the main sources of nonspectral interferences. Significant amounts of carbon and residual acidity in digests may alter the analyte's delivery to the plasma. Furthermore, charge transfer events involving charged species in the plasma that include carbon may impact signal amplification in the presence of a high carbon content[94]. It was also proposed that the inorganic fraction remaining after makeup digests could be the cause of deposits on the interface of the ICP-MS equipment. Moreover, it's critical to remember that substances such as alkaline and

alkaline earth metals may have ionization suppression effects as well as space charge effects, all of which may weaken the analyte signal. Digests containing suspended particles can cause injury to the equipment's introduction systems; however, this disadvantage can be mitigated by filtering the sample. Nonetheless, it is imperative to consider the potential hazards of contamination in addition to the loss of some analytes throughout this procedure. Using an internal standard helps lessen the impact of nonspectral interferences. Internal standards aid in the removal of transit errors and matrix effects between standards solutions and samples. The internal standard should thus be included in samples, standards, and blank solutions. It must also have many of the same properties as the analyte. Instead of using elements that are often undetectable in composition, Sc, Tl, Re, Ga, In, and Rh have been employed as internal standards for the identification of potentially harmful elements, such as Co, Cd, As, Cd, Ni, and Pb[79,87].

Further techniques for correcting non-spectral interferences include matrix-matched calibration, standard addition calibration, and isotope dilution; however, it is crucial to keep in mind that each of these techniques must be thoroughly assessed to reduce the likelihood of obtaining unreliable results[94]. Because of the overlap or close vicinity of emission lines, the resulting extremely complicated spectrum from ICP-OES may contain several spectral interferences. One way to reduce these interferences is to dilute the material or select the best spectral line to use. When atomic or molecular ions are present in ICP-MS that have the same mass to charge (m/z) ratio as the analyte, spectrum interferences might arise. It is feasible to discern between polyatomic ions, oxide ions, and isobaric interference depending on the interfering species[96]. The main causes of polyatomic interferences are the solvent ions, matrix components, and/or plasma gas (Ar). Molecular ions based on argon are a significant cause of disruption. One instance of how high carbon content solutions might result in the synthesis of polyatomic ions is the

production of ^{40}Ar ^{35}Cl with the same m/z of ^{52}Cr[94]. As determination may also be influenced by the formation of ^{40}Ar ^{35}Cl in solutions with a high Cl concentration[94]. A different isotope can be used, mathematical corrections can be applied, collision/reaction cells can be used, instruments can be used in high resolution mode, and alternative introduction systems such as HG, electrothermal vaporization (ETV), and laser ablation (LA) can be used to reduce isobaric and polyatomic interferences[95]. ICP-OES or ICP-MS multielemental detection requires full solubilization of the sample and full matrix digestion. It should be mentioned that as cosmetic samples are known to be somewhat acid resistant, sample preparation may be an important step. Poor sample preparation can reduce the effectiveness of digestion and cause interferences during the determination process.

2.7.4 Other Methods of Determination

The literature lists additional techniques for determining the presence of pollutants in cosmetics. These include linked methods such as ion chromatography (IC), electroanalytical techniques such as potentiometric stripping analysis (PSA), and other spectrometric techniques like cold vapor atomic fluorescence spectrometry (CVG-AFS)[95]. For the purpose of assessing mercury in cosmetics, atomic fluorescence spectrometry (AFS) and chemical vapor generation (CVG) for sample introduction have been proposed[94]. Utilizing the unique spectroscopic characteristics of gaseous atoms to measure analytes, atomic fluorescence spectrometry has grown to be a practical and widely used analytical method[95].

Although numerous AFS spectrometers with distinct sample introduction methods have been documented, CVG-AFS is presently the most popular due to its more sensitive nature and less expensive instrumentation when compared to ICP-MS[95]. When creating gaseous hydrides to study hydride-forming elements like Hg, Cd, As, Pb, Se, Ge, Sb, Zn, Bi, As, and Zn, $SnCl_2$ or

$NaBH_4$ are frequently utilized. When mercury and a reducing agent combine, gaseous mercury also known as cold vapor is produced[95]. Even with all of the benefits, there are a few drawbacks that should be noted. These include the requirement for costly and unstable reagents, interference from transition and noble metals, and a restricted range of elements that can be detected. Electroanalytical stripping techniques like cathodic stripping voltammetry (CSV), PSA, and anodic stripping voltammetry (ASV) have gained interest due to their sensitivity and selectivity in the detection of metal ions[94,95]. Pre-concentration and stripping are the two stages of a stripping analysis. During pre-concentration, the element of interest is accumulated on the working electrode; during the stripping phase, it is stripped off into solution[95].

The primary distinction between stripping voltammetry and PSA is that in the former case, the stripping process involves a spontaneous redox reaction of the working electrode[93,94]. It lessens the possibility that electro-active materials, such as organic molecules, which generate background signals that might overlap the current stripping peak, will interfere with the method. Other benefits that could be mentioned are high sensitivity, selectivity, simplicity, simultaneous determination, and comparatively low cost. Intermetallic complexes, which are vulnerable to the influence of metals that contaminate the matrix, could result from this procedure. Simultaneous Zn, Cd, and Pb in cosmetics evaluation is one application of PSA.

Glassy carbon supports an electrode used in mercury operations[89]. Cosmetics connected to makeup have been found to contain Cr (VI) through the use of spectrophotometric detection and ion chromatography[94,95]. The use of IC methods for measuring Cr (VI) ions is becoming more and more popular in addition to spectrometric methods for speciation analysis (determining Cr (III))[95]. Cr (VI) was measured by spectrophotometric detection and in-column reaction with 1,5-diphenyl carbazide (DPC). When compared to earlier techniques based on high performance

liquid chromatography with UV detection, this approach provides an accurate, straightforward, and sensitive way for the quantification of Cr (VI)[94]. Time and uncertainty are decreased by utilizing a color reagent in a post-column process. Cl and F in eye cosmetics have also been found using ion chromatography with a conductivity detector. This method is particularly vulnerable to interferences from the sample matrix or chemicals used in sample preparation, which may lead to specific issues or prevent the analysis by IC from occurring[95]. The samples need to be diluted multiple times in order to reduce these interferences. It is necessary to apply an adequate sample preparation technique in order to use this determination strategy. This approach should yield a suitable solution with the appropriate LODs to detect the anions fluoride and chloride, respectively. Reduced acquisition and maintenance costs, simplicity of automation, and the absence of costly solvents or gases such as those used for atomic spectrometric procedures involving argon plasma are some advantages of IC[94].

2.7.5 Direct Analysis of Cosmetics

In order to ascertain if nonmetals and metals are present in cosmetics, systems that enable instantaneous analysis have been used in place of sample preparation techniques. Among these, LIBS, EDXRF, HR-CS, GF AAS, and NAA have all been used. Prior research has employed energy dispersive X-ray fluorescence to detect pollutants and important cosmetic ingredients found in makeup[30,95]. One benefit of energy dispersive X-ray fluorescence, a nondestructive analytical method, is that its apparatus is portable[96]. There are several factors to take into account when using the EDXRF as a direct analysis method, such as the impact of moisture content, surface roughness, and particle size and distribution. Even though this method eliminates the sample preparation stage and permits multi-element determination, some challenges may arise since LODs may not be sufficient for the measurement of specific elements at low

concentrations[7,8]. This approach was used to determine the following: K, Ba, Ca, Bi, V, Cu, Zn, K, Mn, As, Rb, Sr, Ti, S, and Fe in lip gloss; Cr, I, Cu, Hg, Bi, Mn, Ni, Pb, Ag, As, V, Mo, Br, Sn, and Cu in eye shadow and lipstick. Over a wide concentration range (from g g^{-1} to mg g^{-1}), EDXRF was usually successful in identifying these elements; however, precision was not evaluated in either scenario. Neutron activation analysis is one technique for element identification in different matrices that is thought to be reliable[96] Comparable to EDXRF, NAA enables multi-element analysis and requires less sample preparation. Nevertheless, NAA takes a long time because the spectrum cannot be obtained for several days following a material's radiation exposure. Nevertheless, depending on the element, interferences may be easily observed, and the LODs produced by NAA may not always be adequate to meet the requirements set forth by the regulatory agencies for subsequent study[94,95].

The main drawback of this approach is the development of radioactive residues, which makes it less prevalent in scientific settings. NAA was only utilized in two investigations that were discovered in the literature to determine the major and trace elements in makeup products like eye shadow and lipstick. In these studies, samples were analyzed without having received any prior care[9,10]. However, sample and standard cooling durations after irradiation varied from one day to four weeks, depending on the analyte. The accuracy was evaluated using CRMs containing inorganic characteristics, like sediments and coal fly ash. Strong agreement with certified values was reached in both cases[9,10]. A short burst of extremely intense radiation from a laser is used in the analytical technique known as "laser induced breakdown spectroscopy" to achieve representative vaporization and excitation of the sample[93,94,95]. The advantages of LIBS are its low sample invasiveness, lack of sample degradation, speed, and capacity for instantaneous analysis without a sample preparation stage. Nevertheless, low accuracy and high

standard deviation results may result from LIBS drawbacks including spectral complexity and representativeness of the small areas the laser pulses sample. The only study using LIBS to identify pollutants in cosmetics was this one. Lead, Cr, Cd, and Zn concentrations in different Saudi Arabian lipsticks were measured. Before the LIBS test, lipsticks were dehydrated (heated to 105 812 C), frozen, and then cut into tiny, 1 cm-diameter circles. Standard samples had been created by combining elemental salts with a lipstick sample that had little contamination (less than the LOD) in order to create calibration curves. After the materials were digested, the findings were compared to those obtained by ICP-OES. It's possible that LIBS isn't the optimal method for determining the safety limits for these elements because the LODs it produced ranged from 1.7 to 2.6 g g^{-1} and are greater than the safe levels recommended by the FDA and EU. For the purpose of detecting mercury in cosmetics, a novel method based on thermal decomposition, gold trap collection, and CVG-AFS detection has been designed and implemented.

In this system, when the mercury compounds and cosmetics matrix degraded at 800 °C, elemental mercury was combined onto a gold trap[121]. Following that, CVG-AFS was used to measure the amount of mercury that had accumulated on the trap. There was a range of agreement with certified values when compared to certified reference materials such as NIST1575a (pine leaves), IAEA (fish tissue), Dorm-2 (fish tissue), and NIST 2709 (soil). In the past few years, high-resolution continuum source graphite furnace atomic absorption spectrometry has proven to be an effective method for directly examining pollutants found in cosmetics related to makeup. The spectrometer comprises a charge-coupled detector, a high-resolution double monochromator including an echelle grating for high resolution, and a continuum radiation source[139]. The ability to identify elements with absorption lines between 190 and 900 nm, the ability to identify elements using molecular absorption spectrometry, which

allows the identification of halogens, and the ability to correct structured background caused by diatomic molecular species are just a few of the advantages this apparatus has over conventional AAS[94]. Talking about the benefits would be beneficial, as they include less contamination and analyte losses and little to no reagent requirement[30,94]. There can be less food produced as a result. A potential limitation that could be brought up is the utilization of low sample masses, which could lead to high standard deviation values because of a lack of homogeneity. Calibration can be difficult since matrix effects often make it impossible to utilize aqueous standard solutions and necessitate the use of CRMs. It is necessary to carefully consider the sample mass, pyrolysis and atomization temperatures, and the use of chemical modifiers for every sample and element[94,95]. As was previously indicated, structured background signal can be produced by diatomic molecular species employing HR-CS GF AAS. This can be addressed by applying the least-squares background correction (LSBC) technique[96].

This is important to know when assessing makeup since these samples' inorganic matrix may provide a background signal that makes it challenging to identify the analytes. This approach was used to detect Sb in eye shadow, and precursors such as SiO_2, a mixture of TiO_2 and SiO_2, zeolite, and mica were taken into consideration for reference spectra creation and background reduction caused by the SiO molecules in the sample. The accuracy of the procedure was evaluated by the utilization of soil CRM analysis and spike tests. The range of spike recoveries was between 82 and 108%, while the range of agreement with certified values was between 97 and 102% when using mica and zeolite as precursors[96]. By using molecular absorption spectrometry (MAS), high-resolution continuum source graphite furnace atomic absorption spectrometry may also be utilized for halogen measurement[97]. F eye shadow recognition has recently been achieved with this approach. By adding 100 g of Ca as a molecule-forming reagent,

employing 1000 °C for pyrolysis and 2400 °C for vaporization, the diatomic molecule CaF was produced[96]. The sediment and copper concentrate CRMs concurred, as did 87–100% of the certified values. The amount of F that can be found in eye shadow is unrestricted even though the LOD is 0.2 g g^{-1}. Procedures must be developed in order to identify other halogens, like Cl, that can irritate and inflame the region surrounding the eyes. Even though this method reduces the sample preparation process, which is an issue for determining the presence of halogens, it is still critical to develop methods for other halogens[96].

2.7.6 Trends and Issues Regarding Toxic and Potentially Toxic Cosmetic Ingredients

Because of the complexity and various composition of organic and inorganic compounds in hair dye solutions, it is challenging to detect potentially harmful and deadly substances and to design an all-inclusive methodology. The precision and accuracy of the proposed methods for elemental assessment in makeup-related cosmetics were not assessed in a number of research that were published in the literature. Aside from the toxicity and risk of the chemicals, sample throughput, analytical procedure complexity, waste production, and costs, other factors should be taken into account while using analytical methods in routine analysis[97].

Numerous studies have examined the necessity of utilizing HF acid in the sample creation of cosmetics used in makeup, as well as the possibility of using alternative complexing acids and diluted acids in this stage, despite the difficulties associated with its use. Since concentrated acids are harmful to the environment and require significant financial outlays to provide adequate waste chemical treatment, more research is necessary. A substantial dilution factor is also required before to the analysis in order to lessen this effect, which occasionally results in LODs that may not be sufficient for the analytical problem[98]. Because of their high residual acidity, the digests can interfere with several analytical procedures. In this instance, utilizing a

variety of analytical techniques to detect additional chemical elements may make the utilization of a combustion process (such as MIC) a feasible substitute for the digestion of cosmetics. When a combustion aid, like microcrystalline cellulose or starch, is included with the sample to encourage the volatilization of the constituents, it can be used to microwave-induced combustion to fully break down organic compounds that are thought to be difficult to digest[95]. It has also been applied to the preparation of inorganic matrix samples[98]. The MIC approach is ideal for elements like halogens that can form unstable species in an acid medium since it allows the user to select the absorbing solution. With MIC's benefits, sample preparation for all kinds of cosmetics can be greatly reduced, making it a great alternative for identifying potentially hazardous ingredients utilizing a variety of analytical methods[95]. Only two research have used the MIC method to identify new halogens in cosmetics.

Furthermore, diluted acid MAWD (with oxygen pressure or with H_2O_2) and microwave-assisted ultraviolet digestion (MW-UV) could be effective procedures for cosmetic sample preparation. These techniques have enabled the efficient digestion of a wide range of substances utilizing diluted HNO_3 as the solution. This is made possible via the MW-UV technique, which combines the use of microwaves and ultraviolet (UV) light. Because UV radiation-induced photochemical reactions create reactive species in the system, they improve the digestive process[95]. In contrast, the diluted acid method of the MAWD approach permits the regeneration of HNO_3 during the digesting stage and, thus, the use of diluted acids throughout the process. This is achieved by either injecting hydrogen peroxide or applying oxygen pressure to digestive tubes. As a substitute for elemental determination in cosmetics, direct analysis of solids has also been suggested due to issues related to the sample preparation phase. Due to matrix effects, CRMs are often necessary, which makes it difficult to apply them in routine analysis. This can also make

the analysis more difficult if there aren't enough CRMs for cosmetics or if the matrix isn't identical[94,95]. This has occurred as a result of issues with sample homogeneity and the calibration procedure. Since the harmful effects of components rely on the species that are present in the sample, a speciation study needs to be done. This should be considered when setting maximum constraints in new official recommendations. Since there aren't many available analytical protocols for this use, new techniques need to be created[97]. Not much research has been done on how to control the quality of cosmetics using additional components, like halogens. Consequently, speciation analysis and halogen determination are popular cosmetics trends. The management of chemical elements in commercially accessible cosmetics, the addition of new limits for other elements and species, and the standardization of chemical element limitations are additional important issues that should be taken into account by official organizations. Accurate analytical equipment should be used by government authorities and cosmetics producers as reference methods for product quality control[96].

2.7.7 Some Reports on Toxicity of Cosmetics and HCPs

The National Cancer Institute formaldehyde cohort study's follow-up data through 1994 led to the 2004 reclassification of formaldehyde (FA) by the International Agency for Research on Cancer (IARC) from a probable (Group 2A) to a known human carcinogen (Group 1). In contrast, the European Chemicals Agency's Committee for Risk Assessment rejected the proposal in 2012 to categorize FA as a known human carcinogen (Carc. 1A), instead suggesting a less protective classification of "substance presumed to have carcinogenic potential for humans" (Carc. 1B)[98]. Though they acknowledge that there is insufficient data to establish a correlation between formaldehyde exposure and NPC56, Marsh and Cols disagree with this most recent decision and recommend that the NCI publications containing data from the 1994 mortality follow-up be re-

analyzed. According to a study, formaldehyde concentrations in BKT goods can be higher than advised and pose a health risk. Industry oversight is required to enhance adherence and safeguard customers and hairdressers[99]. A study used the Comet assay test (single-cell gel electrophoresis) to assess the genotoxic risk to 69 female hairdressers who were regularly exposed to chemicals such as hair dyes, waving and straightening preparations, and manicurist products. The hairdressers' work environment, which involves modifying and inhaling various chemicals on a regular basis, may be linked to their greater frequency of DNA damage. Given that this profession is not formally regulated in many nations, including Brazil, it is plausible that the usage of BKT may have some influence on the data used in this study[100].

An investigation was carried out to assess the possible formaldehyde exposure of clients and salon staff during keratin hair smoothing procedures. The study's findings demonstrate that even "formaldehyde" free professional hair smoothing procedures have the potential to create formaldehyde concentrations that are equal to or higher than the existing occupational exposure limits. Per interquartile rise in concentration, there was an increased risk of Wilms' tumor in infants exposed to formaldehyde, polycyclic aromatic hydrocarbons, perchloroethylene, or acetaldehyde during pregnancy[101].

An association between early-onset leukemia and pregnancy, as well as mother exposure to hair dyes and straightening cosmetics, has been studied[102]. Investigations of homemade formaldehyde-containing hair straightening treatments revealed antibacterial activity in every cream with a favorable mutagenicity induction. They came to the conclusion that there was a strong genotoxic reaction in the creams. The measurement of DNA-protein crosslinks in hospital employees' peripheral blood cells indicates that formaldehyde exposure may cause systemic circulation exposure in humans, with levels ranging from 2.87 ng/g to 12.61 ng/g[102].

Cold vapour fluorescence spectrophotometric analysis was used in research to determine the amount of mercury in soaps in the Gambia; a total of 16 soap brands were examined[103]. Four categories were used to group these soap brands: medicinal, toilet, skin-lightening, and laundry soaps. The soaps were utilized for the analysis; they were bought in the Gambia from various retailers. They demonstrated that the concentration of mercury in all 16 soap brands ranged from 2.87 ng/g to 12.61 ng/g[103]. According to an assessment conducted by the World Health Organization, mercury is frequently present in skin-lightening soaps and lotions, as well as other cosmetics like mascara, cleaning products, and eye makeup[104]. It said that dark-skinned people in Europe and North America, as well as several countries in Africa and Asia, use skin-lightening soaps and lotions more frequently. It went on to say that mercury salts cause lighter skin tones by blocking the production of melanin.

Based on reports from women aged 25, 27, 35, 59, and 77%, the analysis identified the nations in Africa with the highest rates of cosmetic use: Mali, Senegal, South Africa, Togo, and Nigeria. These countries were ranked in order of rising usage by women. In 2004, surveys of women in China, Malaysia, the Philippines, and the Republic of Korea revealed that about 40% of them had used skin lightening treatments. In India, skin lightening products accounted for 61% of the dermatological market[104].

The outcome also revealed that skin-lightening products are made in a number of nations, including the United States, the Dominican Republic, Lebanon, Mexico, Pakistan, the Philippines, and Thailand. Additionally, skin-lightening products containing mercury can be purchased online, and people from Brazil, Kyrgyzstan, Mexico, and the Russian Federation think it's simple to find these products[105]. The results also showed that skin-lightening products come in a variety of forms, such as soap and creams, with the soap having a concentration of roughly

1-3 percent mercury iodide and the cream having a concentration of 1-3% mercury ammonium (some tested soap products had concentrations of up to 31 mg/kg of mercury, while some cream products had concentrations of up to 33,000 mg/kg of mercury)[105].

Endnotes

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Chapter Three

Methodology

3.1 Sample Collection

Five samples of hair-dye brands, popularly used in Ibadan, were bought from different local markets. The samples were numbered from A1 to A5 as shown in Table 3.1.

3.2 Reagents and Materials

Measurements for total concentrations of Silver, Arsenic, Boron, Cerium, Cadmium, Cobalt, Chromium, Cesium, Copper, Iron, Mercury, Magnesium, Manganese, Molybdenum, Nickel, Palladium, Lead, Sulphur, Antimony, Selenium, Silicon and Zinc were successfully carried out on Inductively Coupled Plasma-Optical Emission Spectrometry instrument (ICP-OES) with axial viewing configuration. Unless noted otherwise, every reagent and standard used were ultrapure reagent grade, and Millipore Milli-Q water was used to produce every solution. After being thoroughly cleaned three times with deionized water, all glass and plastic items were immersed in 30% (v/v) HNO_3 for a whole night. Following the soaking process, the plastic and glasses were dried in an oven and rinsed three times using deionized water.

3.3 Sample Pre-treatment and Analysis

The obtained samples were pre-treated using standardized protocols, which included the careful elimination of external pollutants. Hair samples were chopped into the smallest possible bits and immersed in a 5% EDTA solution for 30 minutes after being repeatedly stirred and cleaned three times with a 3:1 v/v ethyl ether/acetone mixture. Following three rounds of rinsing with de-ionized water, the samples were dried at 80 °C to a consistent weight and placed in polyethylene bags for storage.

Table 3.1: Selected Hair Dyes from Different Manufacturers

Sample	Brand	Colour	Manufacturer	Country of Origin
A1	Cruset	Black	Guangzhou Rainbow Cosmetic	Thailand
A2	Tovchcolor	Green	Guangzhou Chenyi Biotechnology Ltd	China
A3	Subaru	Gold	CNGuangzhou Yucaitang Cosmetics Co., Ltd	China
A4	Subaru	White	CNGuangzhou Yucaitang Cosmetics Co., Ltd	China
A5	Subaru	Wine red	CNGuangzhou Yucaitang Cosmetics Co., Ltd	China

Cruset (black dye), Tovchcolor (green dye), Subaru (gold dye), Subaru (white dye) and Subura (wine red dye)
Source: Author's Analysis, 2024

To 1 g of each sample of the brand-name hair dyes, approximately 5 ml of HNO3 (nitric acid) was added. To ascertain the concentration of Ag, As, Boron, Cerium, Cadmium, Cobalt, Chromium, Cesium, Copper, Iron, Mercury, Magnesium, Manganese, Molybdenum, Nickel, Palladium, Lead, Sulphur, Antimony, Selenium, Silicon, and Zinc, the sample was heated for four hours at 85 °C, cooled to room temperature, and then injected into an Inductively Couple Plasma-Optical Emission Spectrometry (ICP-OES).

3.4 Analytical Methods

An analytical weighing balance was used to precisely weigh 0.5 g of the prepared samples, which were then transferred to a screw-cap Polytetrafluoroethylene digestion tank. After adding

2 mL of nitric acid and 1 mL of 30% hydrogen peroxide, the mixture was allowed to predigest for 12 hours at room temperature. The pots were sealed and left in a 160°C oven for 4 hours. The pots were allowed to cool to room temperature when the digestive process was finished. The digest was prepared for ICP-OES analysis by diluting it with 10 mL of Milli-Q water. 1 mL of the diluted solution was added to a 5 mL vial for the measurement of Cd, Cu, Pb, As, Hg, Sb, and Ni. Next, 1 mL of 5% thiocarbamide and 3 mL of 10% nitric acid were added, and the mixture was allowed to react for 5 hours at room temperature.

3.5 Quality Assurance and Statistical Analysis

Prior to being cleaned with deionized water, every piece of glassware utilized in this investigation was immersed in a 10% nitric acid solution for 24 hours. Every ten runs, the instrument was calibrated. Using spike recovery techniques, the analytical procedure's accuracy was confirmed in the absence of a certified reference material. All analytical procedures, from digestion to ICP-OES analysis, were performed after a known quantity of the test elements at three concentration levels was added to new portions of previously examined samples.

The metals' percent spike recoveries ranged from 83.4 to 105%, and the calibration precisions within and between days were less than 13%. Following preparation, a nebulizer was used to deliver the sample into the device, and it was read under the suggested circumstances. Table 3.2 lists the circumstances under which the PTEs analysis was carried out. The SPSS 13.0 program (SPSS Inc., Chicago, IL, USA) was used to process and analyze the statistical data. The student’s t-test will be used to examine the gender differences in the concentration of the chosen heavy metals in scalp hair. To look into the connection between age and the levels of heavy metals found in hair, the Pearson's correlation coefficient was computed. Additionally, linear regression analysis will be used to measure the correlations between age and hair heavy metal levels. One-

way ANOVA (Analysis of Variance) was used to examine the variations in heavy metal concentrations in hair among age groups. Statistical significance was defined as a p-value of less than 0.05.

3.6 Non-carcinogenic Exposure Assessment and Risk Characterization

The lifetime average daily dose (LADD) was used to assess this risk through the ingestion, inhalation, and cutaneous pathways[8]. 250 adult male and female residents of Southwest LGA, Ibadan, were given questionnaires to complete in order to assess the exposure levels to PTEs caused by the use of hair dyes. Important factors were questioned, including weight, age at first use, frequency, and duration of hair dye use.

Table 3.2: Recommended Conditions for Analysis on ICP-OES

Element	Flame	Wavenumber (nm)	Burner	Calibration method	Stock standard solution
Ag	Argon plasma	328.068	5 cm	Linear	1,000 µg/ml
As	Argon plasma	188.980	5 cm	Linear	1,000 µg/ml
B	Argon plasma	249.678	5 cm	Linear	1,000 µg/ml
Ce	Argon plasma	446.021	5 cm	Linear	1,000 µg/ml
Cd	Argon plasma	214.439	5 cm	Linear	1,000 µg/ml
Co	Argon plasma	228.615	5 cm	Linear	1,000 µg/ml
Cr	Argon plasma	205.560	5 cm	Linear	1,000 µg/ml
Cs	Argon plasma	459.311	5 cm	Linear	1,000 µg/ml
Cu	Argon plasma	324.754	5 cm	Linear	1,000 µg/ml
Fe	Argon plasma	238.204	5 cm	Linear	1,000 µg/ml
Hg	Argon plasma	194.164	5 cm	Linear	1,000 µg/ml
Mg	Argon plasma	279.553	5 cm	Linear	1,000 µg/ml
Mn	Argon plasma	257.610	5 cm	Linear	1,000 µg/ml
Mo	Argon plasma	202.032	5 cm	Linear	1,000 µg/ml
Ni	Argon plasma	216.555	5 cm	Linear	1,000 µg/ml
Pd	Argon plasma	229.651	5 cm	Linear	1,000 µg/ml
Pb	Argon plasma	220.353	5 cm	Linear	1,000 µg/ml
S	Argon plasma	180.669	5 cm	Linear	1,000 µg/ml
Sb	Argon plasma	217.582	5 cm	Linear	1,000 µg/ml
Se	Argon plasma	203.985	5 cm	Linear	1,000 µg/ml
Si	Argon plasma	251.611	5 cm	Linear	1,000 µg/ml
Zn	Argon plasma	202.548	5 cm	Linear	1,000 µg/ml

Dilution = 20

Source: Author's Analysis, 2024

Besides, Equation 3.1 was used to determine the PTEs intake through skin exposure to hair dyes.

$$D_{dermal} = \frac{C \times SA \times SL \times ABS \times EF \times ED}{BW \times AT} \times 10^{-6} \quad \textbf{Equation 3.1}$$

Where; D_{derm} (ppm kg^{-1} day^{-1}) = average daily intake of heavy metals through skin exposure to hair dyes.

C (ppm kg^{-1}) = metal concentration in hair dye

SA (cm^2) = the skin area of scalp

SL (mg cm^{-2}) = skin absorption factor

ABS (unitless) = the depth absorption skin factor

EF (day $week^{-1}$) = exposure frequency

ED (year) = exposure duration

BW (kg) = body weight

AT (day) = average time[1,2]. AT parameter is obtained using Equation 3.2.

$$AT = ED \times 14 \quad \textbf{Equation 3.2}$$

The chronic risk was determined using chronic daily intake (CDI) and hazard quotient (HQ) index, based on the modified equation using[3,4]:

$$CDI = (C \text{ X } DI)/BW \quad \textbf{Equation 3.3}$$

Where; CDI = human exposure risk through the ingestion or inhalation of hair dyes pathway (ppm/day),

C = concentration of heavy metal in hair dyes in mg L^{-1}

DI average daily intake rate (2.0 L Day^{-1} $person^{-1}$)

BW = body weight (72 kg for adults)[1]

Where; ED (year) = number of years that hair dyes are consumed. Besides, by considering the available information non-carcinogenic health risk effects were evaluated through Equation 3.4.

$$HQ = \frac{Ddermal}{RfD} \qquad \textbf{Equation 3.4}$$

Where RfD (mg $kg^{-1}day^{-1}$) = Reference Dose and HQ (unitless) is Hazard Quotient. Moreover, HI (chronic hazard index) is obtained by Equation 3.5, used to sum more than one HQ resulted from different elements or from different pathways[4].

$$Chronic\ Hazard\ Index = \sum_{k=1}^{n} \frac{Ddermal}{RfDk} \qquad \textbf{Equation 3.5}$$

3.7 Carcinogenic Analysis

By calculating the LCR using Equation 3.6, the carcinogenic analysis is carried out by assessing the likely cancer risks associated with PTE exposure[5]. The LCR is actually the likelihood that an individual would get any kind of cancer over their lifetime due to exposure to a specific daily quantity of a carcinogenic substance for 70 years, 24 hours a day[6,7]. The permissible limits of LCR for one or more PTEs are $10^{-6} < LCR < 10^{-4}$ [8].

$$\textbf{LCR} = \textbf{CDI} \times \textbf{CSF} \qquad \textbf{Equation 3.6}$$

The cancer slope factor, or CSF (ppm/day), is contaminant specific and is the risk resulting from an average lifetime exposure to one carcinogen chemical. Specifically, mercury does not have a CSF since it is not thought to induce cancer.

Endnotes

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Chapter Four

Results and Discussion of Findings

4.1 PTEs Concentration in Hair Dye Products (HDPs)

Five distinct hair dye brands that are frequently used in Ibadan, Nigeria, were measured and analyzed for PTE levels that differed significantly from one another at $p < 0.05$. Ag, As, B, Ce, Cd, Co, Cr, Cs, Cu, Fe, Hg, Mg, Mn, Mo, Ni, Pd, Pb, S, Sb, Se, Si, and Zn were among the 22 PTEs whose quantities were measured in the five hair dye samples. These products' carcinogenic, non-carcinogenic, and dermal sensitivity health risk assessments were then examined. The studied PTEs concentrations were ranged as; Cs > Mg > Si > Fe > Pd > Pb > Ag > Zn > Mn > Se > Ni > Ce > Sb > As > Cr > B > Cu > Mo > Co > Cd > S > Hg respectively.

According to Figure 4.2, the amounts of Ag in each product ranged from 1.02 to 1.43 ppm, with the highest concentration found in A1 (black dye) and the lowest in A4 (gold dye). The most serious health effect of Ag exposure, according to the Centers for Disease Control and Prevention (CDC) and numerous other specialists, is skin coloring, which is evident in argyria[1]. Breathing issues, throat and lung discomfort, and stomach pain can result from exposure to hair dyes that contain relatively high concentrations of Ag compounds, such as AgO or $AgNO_3$.

As part of the guidelines for their safe use, the USFDA has established limitations for the amount of Ag that can be present in color additives. The typical range of permitted limits is 0.10 to 0.20 ppm[2]. However, there is a lack of research on PTEs of Ag in hair dyes. The concentration of As in hair dye brands was determined to be between 0.24 and 0.3 ppm, as shown in Figure 4.3. The As concentration is significantly higher in the A1 (black) dye brand than in the A2 (green) dye brand, which has the lowest concentration range. The USFDA has set a 3 ppm allowed limit for As in powder and other cosmetic goods, meaning that all of the hair color brands examined in

this study had As at a level below that limit[3]. The levels in hair shampoo ranged from traces (0.252 ppm) to high amounts (0.087 ppm)[4]. When compared to previous published studies, the concentration values were deemed low[4]. Long-term inhalation exposure can cause gastrointestinal tract and urinary system malignancies, circulatory and peripheral nervous system abnormalities, certain skin impacts, and an elevated risk of lung cancer. While only a small quantity of As(V) penetrated cell membranes via an energy-dependent transport pathway before being instantly reduced to As(III), the majority of As enters the body in the As(III) form[5]. According to the IARC, arsenobetaine and other organic As-compounds are not classifiable with regard to their carcinogenicity to people (Group 3); dimethylarsinic acid and monomethylarsonic acid are possibly carcinogenic to humans (Group 2B); and inorganic As are carcinogenic to humans (Group 1)[6].

Although the boron used in hair dyes is safe, if someone inadvertently drinks hair dyes containing borax (sodium borate) or boric acid, they could be harmed. Excess boron can cause headaches, seizures, rashes, nausea, vomiting, and diarrhea. Excessive levels of boron can be fatal. The measured boron concentration ranged from 0.18 to 0.4 ppm, with an average of 0.29 ppm, as shown in Figure 4.4. In order to ensure the safe use of color additives, the USFDA has established limitations for boron as an impurity[3]. The typical range of permissible limits is 10–20 ppm. When compared to the USFDA limits, the concentration readings were deemed modest[4]. However, the amount of boron in hair colors has not been reported.

As shown in Figure 4.5, the Cerium concentrations in our samples ranged from 0.04 to 1.02 ppm. A1 brand (black dye) had the highest Ce concentration, whereas A4 brand (white dye) had the lowest concentration. The main reason Ce is hazardous in the workplace is because gasses and moisture can be breathed through the air. Lung embolisms may result, particularly with

prolonged exposure. When cerium builds up in the human body, it might endanger the liver. Ce in hair dyes is permitted at a maximum of 0.0027 parts per million[3]. The range of the Cd content was 0.02 to 0.05 ppm. As seen in Figure 4.6, the Cd concentrations of green (A3) and gold (A4) hair colors were higher than those of the other hues examined. The USFDA authority has set a maximum acceptable level of 3.00 ppm for Cd as an impurity in hair dye products[2]. The HDP concentrations in these samples were below the regulatory control limits set by the USFDA. There were reports of Cd values in Nigerian HCPs ranging from 2.58 to 6.95 ppm[7]. A study discovered <0.002 ppm in shampoos and conditioners[4].

Cd values of 0.033–0.042 ppm was recorded in another investigation[8]. Cd levels in hair treatments ranged from 4.2 to 6.8 parts per million, according to one investigation[7]. Our samples had lower Cd amounts than some of the previously reported levels. Nevertheless, compared to our samples, other research on HCPs showed lower levels.4. According to the International Agency for Research on Cancer, cadmium is "carcinogenic to humans," and the US Department of Health and Human Services has classified its compounds as human carcinogens[6].

While prolonged exposure to low levels of cadmium can cause kidney damage, bone deformities, and the tendency for bones to break readily, high amounts of cadmium can cause severe stomach irritation, vomiting, and diarrhea[7]. Only a small percentage of the metals consumed by humans and animals are really retained in the body; the majority are eliminated. Cd is a strong cell toxin that can harm cells in a variety of ways, such as causing them to die or proliferate more quickly. Children may experience neurological disorders like learning impairments and hyperactivity as a result of its effects on the nervous system. Cd causes oxidative stress in brain cells, which damages proteins and leads to neurodegeneration. Cd does not need to be abundant in items to cause hypertension, as it can be found in a variety of hair dyes[8].

In Figure 4.7, the Co concentrations in these HDPs varied from 0.003 to 0.04 ppm. The dye A5 (wine) has the highest amounts of Co. The lowest quantities of Co were found in black dye (A1). In Ghana, hair pomades had cobalt concentrations ranging from 10.667 to 25.350 ppm[7]. Our samples' Co concentrations were lower than those of Ghanaian HCPs. The 2008 patch test of 25,000 European individuals revealed a positive response in 7.9% of cases, confirming that cobalt is a skin allergen that causes allergic contact dermatitis (ACD). Sweat's ability to oxidize is directly correlated with the flow of Co ions through the skin[9]. Itching and eczematous periungal and palmar sores are documented side effects of Co exposure[10]. Based on these results, it was suggested that cosmetics intended for skin application should either contain Co at concentrations below 1 ppm or, for increased skin protection, should not contain Co at levels above 5 ppm[2]. However, no Co amounts above 1 ppm, which is recommended for increased skin protection, were found in any of the examined samples[2].

The Cr concentration in each of the five samples is displayed in Figure 4.8. The findings showed that the greatest value (0.767 ppm) was found in A3 (gold dye), followed by A4 (white dye) at 0.318 ppm, wine dye (A5) at 0.202 ppm, green dye (A2) at 0.185 ppm, and black dye (A1) at 0.005 ppm. Every sample that was examined fell within the USFDA's guidelines[2]. One study found that hair dyes from South-South Nigeria contained 2.5 – 4.2 ppm of Cr, whereas another study found 0.43 – 4.9 ppm in the Federal Capital Territory (FCT) in Abuja, Nigeria[11,12]. The metal's oxidation state determines how hazardous chromium compounds are. Compared to trivalent form, hexavalent form is more hazardous. Hexavalent chromium (Cr^{+6}) causes skin allergies and corrosion. The International Agency for Research on Cancer lists Cr^{+6} compounds as carcinogenic[13]. Because of its high solubility, Cr^{+6} penetrates the skin more than Cr^{+3}. The contact time has an impact on the pace at which Cr penetrates the skin[11]. Skin irritation or

ulceration, allergic contact dermatitis, occupational asthma, nasal irritation and ulceration, perforated nasal septa, rhinitis, nosebleed, respiratory irritation, nasal cancer, sinus cancer, eye irritation and damage, perforated eardrums, kidney damage, liver damage, pulmonary congestion and edema, epigastric pain, and tooth erosion and discoloration are among the adverse health effects linked to hexavalent chromium exposure[12]. Cesium is the most prevalent metal in these HDPs, with concentrations ranging from 0 to 22561.9 ppm, as shown in Figure 4.9. White dye (A4) has the greatest Cs among the hair dye brands examined, while gold (A3) has no levels of Cs. Large doses of radioactive Cs can harm human cells due to radiation exposure. Acute radiation syndrome, which includes unconsciousness, hemorrhage, nausea, vomiting, diarrhea, and in extreme circumstances, death, may also occur. Between 900 and 1000 parts per million is the upper limit for Cs in hair dyes[2]. With the exception of A3 (gold), which has no traces, every sample examined in this study had a significantly higher concentration of Cs.

As seen in Figure 4.10, copper was found in trace amounts in the brands of HDPs under investigation at quantities between 0.032 and 0.066 ppm. A4 (black dye) has the highest concentration of Cu. The amounts of Cu in HCPs have been documented in comparatively few research. For example, research discovered that shampoos sold in Pakistan had Cu amounts ranging from 0.071 to 2.387 ppm, whereas HCPs in Ghana had Cu contents between 0.70 and 12.80 ppm[7,13]. Although copper is a necessary component of both human and animal diet, its use in intrauterine devices (IUDs) has been linked to women increased menstrual blood and pain[15].

The hair dye brands' iron contents were also ascertained. The studied samples had an average Fe concentration of 7.5128 ppm, with a range of 2.361 to 21.258 ppm, as shown in Figure 4.11. In contrast to our results, the average Fe content in hair pomade was found to be 209.8 ppm14. Fe-related side effects in the human body include headache, nausea, vomiting, dizziness, anorexia,

and weight loss[10]. Furthermore, because of the quick catalysis of oxygen radicals in cells, elevated Fe levels raise the possible risk of cancer[15]. The hair dye brands' mercury contents were also ascertained. The average Hg concentration found in all tested hair dyes ranges from -0.12 to 0.119 ppm, as shown in Figure 4.12. With a concentration of 0.119 ppm, A4 (white dye) has the highest Hg content, while A3 (gold dye) has the lowest concentration range (-0.12 ppm). One part per million is the USFDA's allowable level for Hg[6]. According to the results, two brands under investigation had trace amounts of mercury. All of the samples with detectable mercury contents were found to be below the USFDA's allowable levels[2]. Additionally, the research's findings fall short of those of the earlier study.

Acute or long-term exposure to topical mercury salts can cause renal, neurological, and skin damage, even though the IARC has not classified metallic or inorganic mercury compounds as carcinogenic to humans (Group 3)[6]. There have been reports of cutaneous abnormalities such as purpura, erythroderma, gingivostomatitis, flushing, grey or blue-black facial discolouration, burning of the face, and contact dermatitis. Furthermore, high urinary Hg concentrations (>20 ppm) have been linked to symptoms of mercury poisoning. Inorganic Hg salts are also easily absorbed through the skin and eliminated mainly by the kidneys[4]. According to Figures 13 and 14, the concentrations of manganese and magnesium in these samples varied from 0.34 to 1.55 ppm with an average of 0.786 ppm and 30.88 to 902.18 ppm with an average of 206.572 ppm. While A1 (black) had the highest Mn content, A4 (white) had higher Mg concentrations than other brands. Mg and Mn have USFDA-permissible limits of 30 and 0.1 ppm, respectively[6]. According to an analysis, hair pomades in Ghana had an average Mn concentration of 9.8 ppm[7].

The HDPs' molybdenum contents were also ascertained (Figure 4.15). A3 had the highest Mo concentration (0.178 ppm), whereas A4 had the lowest concentration (-0.12 ppm). The USFDA

recommends 0.1 ppm of Ni and Mo in cosmetics[2]. Nonetheless, it is recommended that HDPs with a Mo concentration of less than 1.0 ppm be used for skin protection, especially those that come into close contact with the skin, as 0.5 ppm of Mo concentration is sufficient to induce dermatitis[10]. Figure 4.16 shows the Nickel amounts in the several hair dyes that were examined. They are as follows: A4 (0.92 ppm) > A3 (0.776 ppm) > A1 (0.633 ppm) > A3 (0.588 ppm) > A5 (0.00 ppm). Ni had a USFDA-permissible limit of 5 ppm[2]. An experiment that found 0.83 to 3.11 ppm of Ni in FCT-Abuja, Nigeria, and another that found lower values of 1.5 to 7.5 ppm in hair dyes from South-South Nigeria are both consistent with the findings of this study[11,12]. When nickel comes into contact with perspiration on human skin, it can oxidize to create soluble and diffusible chemicals that can enter the stratum corneum by intracellular, transcellular, or appendageal pathways.

The counter ions (acetate, chloride, nitrate, and sulphate), sweat's oxidizing ability, sex (male or female), exposure duration, and dosage are some of the variables that affect the nickel diffusion rate, which is limited to less than 1 %. Given how long cognitive materials are in touch with the skin, there may be a higher risk of developing allergic dermatitis[16]. In HDPs, palladium concentrations were also examined. According to Figure 4.17, A2 had the highest palladium content (2.611 ppm), whereas A5 had the lowest amount (0.301 ppm). Our samples measured Pd levels fell under the USFDA's regulation threshold of 20 ppm[2]. Furthermore, the range of Pd concentration in hair dye samples was nearly identical to the level that had been previously reported[8]. The Lead concentration in the hair dyes under study is displayed in Figure 4.18. The Pb levels that were measured varied from 0.468 to 1.932 ppm. A2 had the lowest Pb levels (0.468 ppm), while A4 had the highest (1.932 ppm), followed by A1 (1.414 ppm) and A5 (1.118 ppm). Our samples measured Pb concentrations fell below the USFDA's 20 ppm regulation

limits[2]. All of the hair color products' Pb levels fell within the USFDA's maximum allowable limit (10 ppm) for external cosmetic usage. According to one analysis, South-South Nigerian hair dyes included 0.5–28 ppm of lead[11]. This investigation revealed lower concentrations than a previous study that reported ranges between 0.43 and 1.3 ppm in FCT-Abuja, Nigeria[12]. Pb contamination of black hair colors can occur when contaminated raw materials or Pb -containing pigments are used. Every day, Pb comes into touch with the skin, and part of it is absorbed through the skin[8]. High levels of Pb exposure can harm the nervous system, which can lead to kidney damage and brain disorders. Because it can easily pass through the placenta and enter the fetal brain, pregnant women and small children are especially at risk. Additionally, it can be kept in bones and passed on to babies through breastfeeding. Additionally, miscarriages, hormonal abnormalities, decreased fertility in both men and women, irregular menstruation, and delays in the onset of puberty in girls have all been connected to Pb exposure[8]. According to reports, 33 % of lead that enters a child's body and 99 % of Pb that enters an adult's body are eliminated in roughly two weeks[8].

HDPs were used to assess sulfur (Figure 4.19). The range of the measured S levels was -0.38 to 0.06 ppm. A5 had the highest S concentration (0.06 ppm), whereas A1 had the lowest (0.38 ppm). Our samples' measured S and Sb levels fell below the USFDA's regulation limitations of 5.00 ppm and 5.00 ppm, respectively[2]. According to Figure 4.20, A4 had the highest antimony concentration (1.29 ppm), whereas A5 had the lowest (-0.11 ppm). Our samples' measured Sb levels fell below the USFDA's regulation limits, which are 5.00 ppm, respectively[2]. Sb absorption through the skin has not been thoroughly investigated; an in vitro percutaneous investigation suggested that 0.26 % of Sb trioxide is absorbed through human skin[17]. When antimony sulfide became uncommon, Pb sulfide and Pb oxide took its place. Antimony sulfide

was used in cosmetics like rouge and black paint for eyebrows. Samples made in Egypt showed that only one sample of compact face powder had a comparatively high Sb content (5.36 ppm)[18]. Cosmetics made in Japan, such as soaps (< 0.177 ppm) and bronzing face powders (< 0.46 ppm), had low amounts of Sb[19]. The highest Sb concentrations, ranging from 0.012 to 0.21 %, were found in kohl samples (both branded and unbranded) gathered from six different regions of Saudi Arabia. These levels corroborated the findings that Sb sulfide was present in previous varieties of kohl[18]. Compared to earlier findings, our samples are significantly smaller.

The HDPs' selenium levels were also measured (Figure 4.21). A2 had the highest concentration of Se (1.21 ppm), whereas A4 had the lowest concentration (0.18 ppm). It was observed that our samples' Se concentration was similar to that of earlier findings[20]. The USFDA recommends 1 ppm of selenium in cosmetics[2]. Nonetheless, it is recommended that the content of Se in HDPs be less than 1.0 ppm for skin protection.

Hair loss and nail brittleness or loss are the most prevalent clinical indicators of selenosis, or chronically excessive selenium consumption. Skin rash, nausea, diarrhea, exhaustion, irritability, and anomalies of the nervous system are other symptoms. The HDPs' silicon contents were also ascertained (Figure 4.22). A5 had the highest concentration of silicon (140.98 ppm), while A3 had the lowest (130.45 ppm). The USFDA recommends 10 ppm of Si in cosmetics[2]. Nonetheless, it is recommended that the content of Si in HDPs be less than 1.0 ppm for skin protection. On touch, silicon irritates the skin and eyes. Inhalation will irritate the mucous membranes and lungs. Redness and wetness of the eyes are signs of eye irritation. Skin inflammation is characterized by reddening, scaling, and itching[8]. Zinc and hydrogen peroxide, as well as other substances or mixes that release hydrogen peroxide, such as carbamide peroxide as zinc peroxide, are found in hair dyes. Our samples had Zn values ranging from 0.61 to 1.87 ppm (Figure 4.23). Zinc is

present in all samples in varying amounts; the highest concentration (1.87 ppm) was found in A2

Parameters	A1	A2	A3	A4	A5

(black dye), which did not above the USFDA restriction of 12 ppm, while the lowest concentration (0.61 ppm) was found in A5[2,3]. Overexposure to zinc can be harmful. High amounts of zinc in the hair are very uncommon and may be a sign of a zinc overdose. Excess zinc can cause gastrointestinal problems, tachycardia, impaired vision, hypothermia, and diminished heme synthesis (copper insufficiency)[8].

4.2 Comparison of Different Color Brands to Concentration of PTEs in Hair Dyes

Figures 4.1 showed the levels of concentrations of potential toxic elements in hair dye A1 to A5 in comparison to different color brands. A1 is comprises of black dye, A2 (green dye) A3 (gold dye) A4 (white dye) and A5 (wine dye). A4 (white dye) has highest average PTEs concentration of 1074.149 ppm, followed by A1 (black dye) with an average concentration of 882.715 ppm. A5 (wine dye) contains an average PTEs concentration of 720.246 ppm, followed by A2 (green dye) which has 689.242 ppm average concentration. A3 (gold dye) has the lowest average PTEs concentration of 7.845 ppm. It was observed that Ce, Mg and Si concentrations were all higher in all the HDPs. Hg was found in trace amounts in A4 and A5, with concentrations of 0.119 and 0.001 ppm, respectively, which are below allowable limits, but not in A1, A2, or A3. With a concentration of 0.06 ppm, A5 was the only hair dye brand that contained Sulphur. Sb was found in two brands (A1 and A5) in concentrations of 0.52, 1.29, and 0.33 ppm, respectively, although it was not found in A3 or A3. A1 and A4 have significantly greater Fe concentrations than A2, A3, and A5.

(ppm)					
Ag	1.430[a]	1.120[b]	1.020[d]	1.080[c]	1.070[c]
As	0.300[b]	0.240[e]	0.290[c]	0.260[d]	0.640[a]
B	0.250[d]	0.400[a]	0.290[c]	0.330[b]	0.180[e]
Ce	1.020[a]	1.000[b]	0.090[d]	0.040[e]	0.140[c]
Cd	0.020[c]	0.050[a]	0.050[a]	0.040[d]	0.030[b]
Co	0.003[e]	0.020[d]	0.055[b]	0.130[a]	0.040[c]
Cr	0.005[e]	0.185[d]	0.767[a]	0.318[b]	0.202[c]
Cs	19232.900[b]	14991.200[d]	0.000[e]	22561.900[a]	15661.400[c]
Cu	0.606[a]	0.080[c]	0.032[d]	0.146[b]	0.080[c]
Fe	7.719[b]	2.361[e]	3.411[c]	21.258[a]	2.815[d]
Hg	-0.311[d]	-0.263[d]	-0.120[c]	0.119[a]	0.001[b]
Mg	33.460[c]	31.650[d]	30.880[e]	902.180[a]	34.690[b]
Mn	1.550[a]	0.400[d]	0.340[e]	1.220[b]	0.420[c]
Mo	0.157[b]	0.178[a]	0.112[c]	-0.120[e]	0.076[d]
Ni	0.633[c]	0.588[d]	0.776[b]	0.920[a]	0.000[e]
Pd	0.370[d]	2.611[a]	1.588[c]	2.009[b]	0.301[e]
Pb	1.414[b]	0.468[e]	0.760[d]	1.932[a]	1.118[c]
S	-0.380[b]	-0.570[c]	-0.390[b]	-1.340[d]	0.060[a]
Sb	0.520[e]	-0.280[d]	-0.110[c]	1.290[a]	0.330[b]
Se	0.480[c]	1.210[a]	1.180[b]	0.180[e]	0.250[d]
Si	135.730[c]	133.890[d]	130.450[e]	136.150[b]	140.980[a]
Zn	1.870[a]	0.790[d]	1.120[c]	1.240[b]	0.610[b]

Table 4.1: PTEs Concentration in HDPs

Values are in ppm. a, b, c, d means along the same row with different superscripts are significantly different (P<0.05)

Source: Author's Analysis, 2024

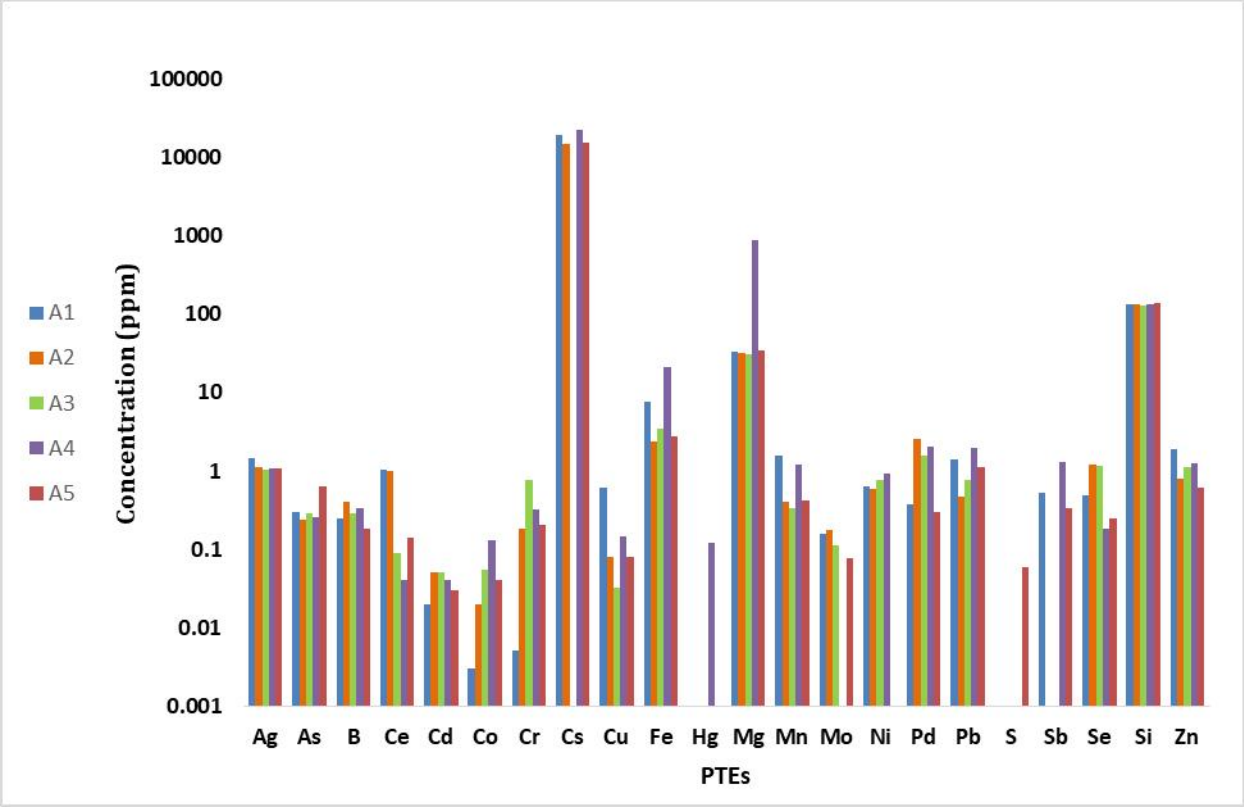

Figure 4.1: Comparison of Different Color Brands to Concentration of PTEs in Hair Dyes
Source: Author's Analysis, 2024

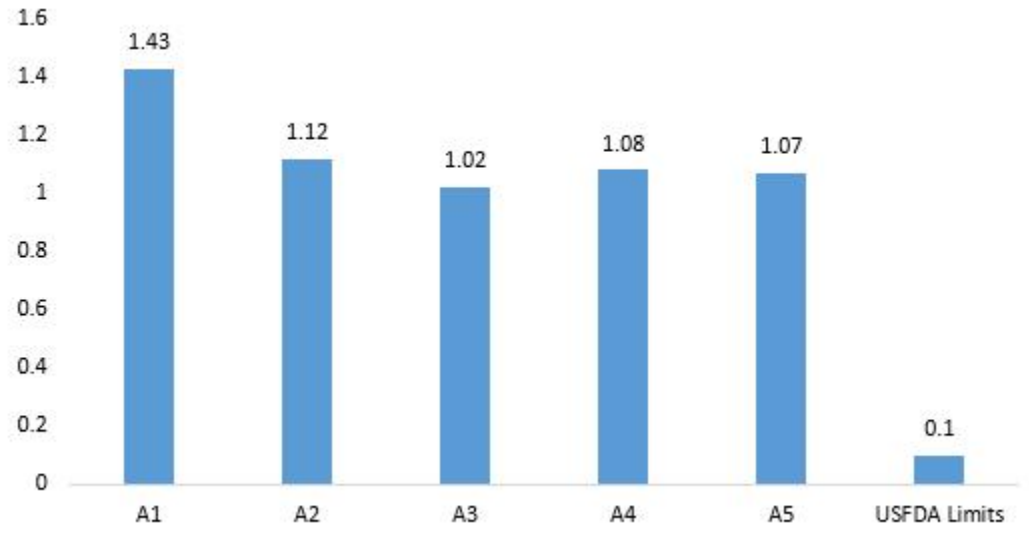

Figure 4.2: Level of Silver in different type of hair dyes
Source: Author's Analysis, 2024

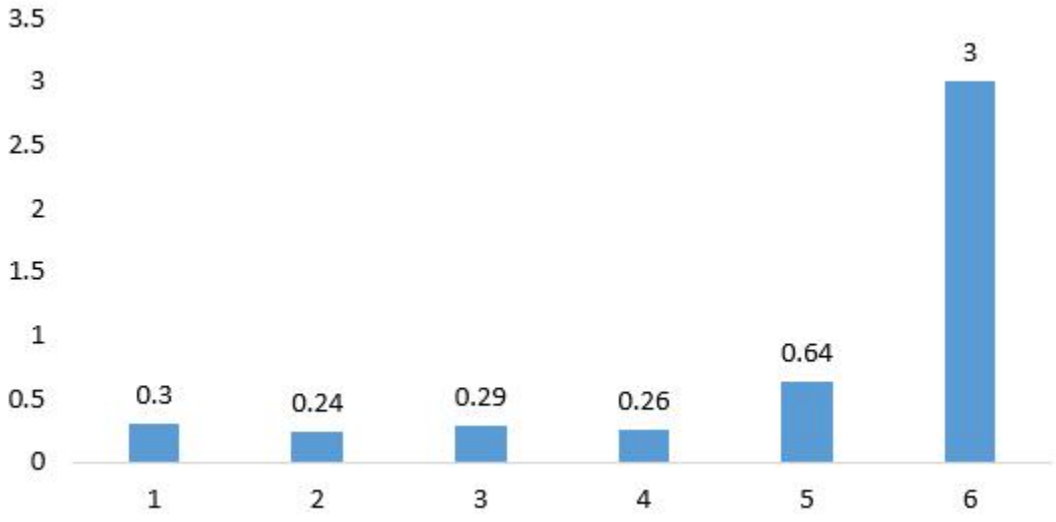

Figure 4.3: Level of Arsenic in different type of hair dyes
Source: Author's Analysis, 2024

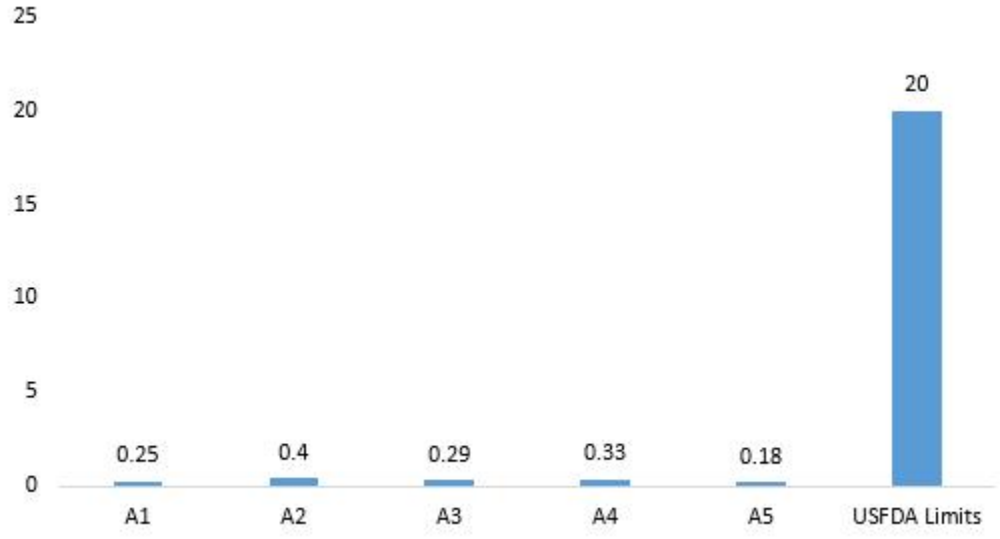

Figure 4.4: Level of Boron in different type of hair dyes
Source: Author's Analysis, 2024

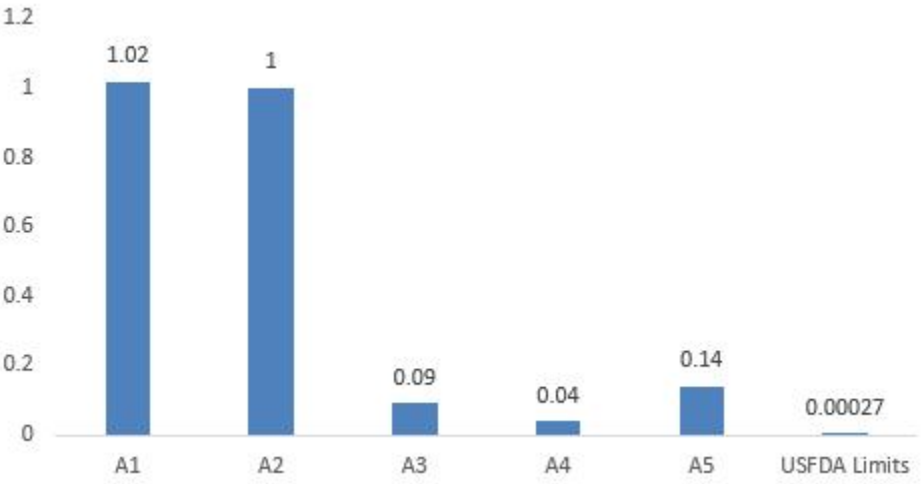

Figure 4.5: Level of Cerium in different type of hair dyes
Source: Author's Analysis, 2024

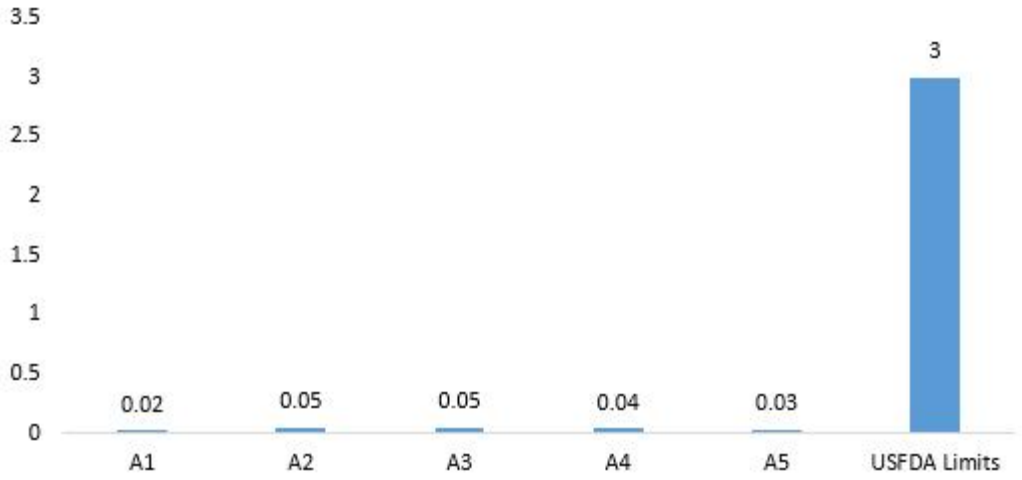

Figure 4.6: Level of Cadmium in different type of hair dyes
Source: Author's Analysis, 2024

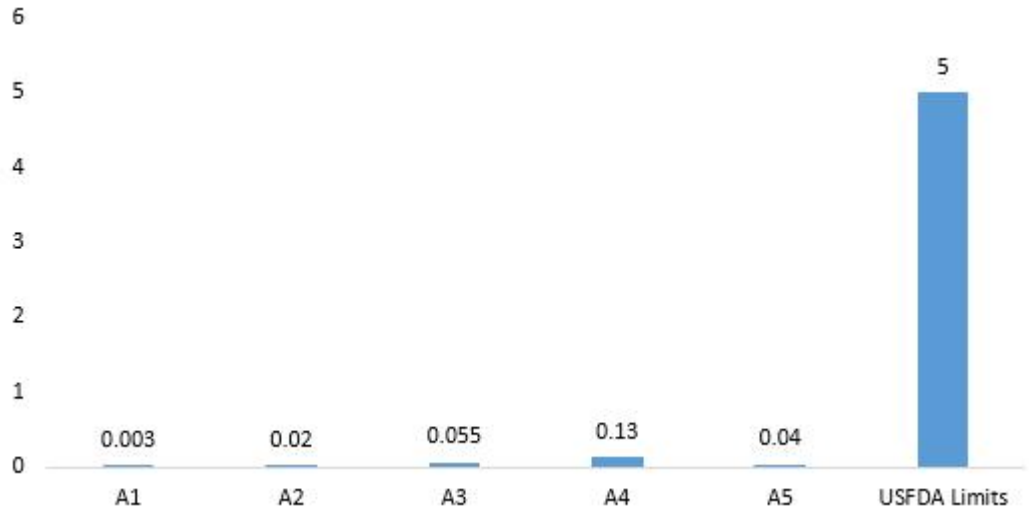

Figure 4.7: Level of Cobalt in different type of hair dyes
Source: Author's Analysis, 2024

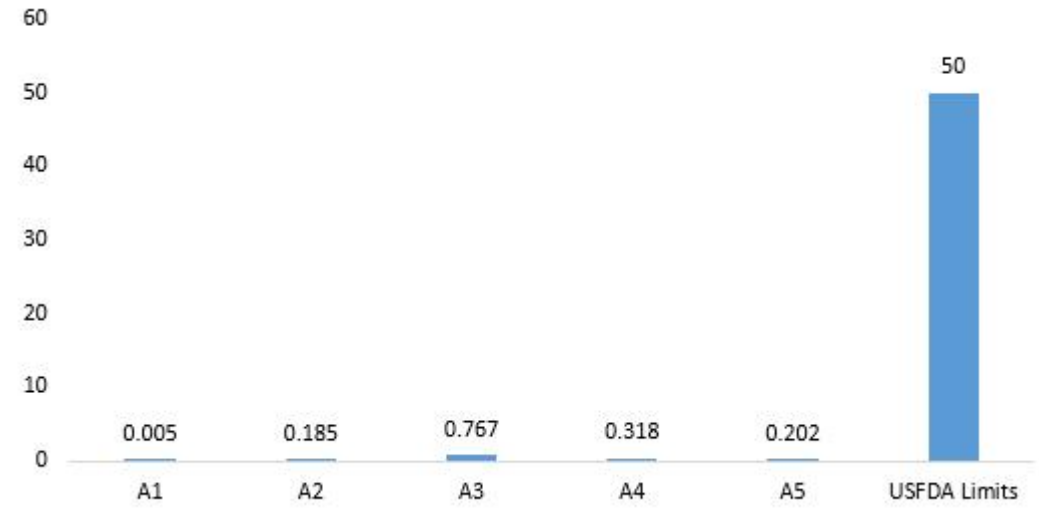

Figure 4.8: Level of Chromium in different type of hair dyes
Source: Author's Analysis, 2024

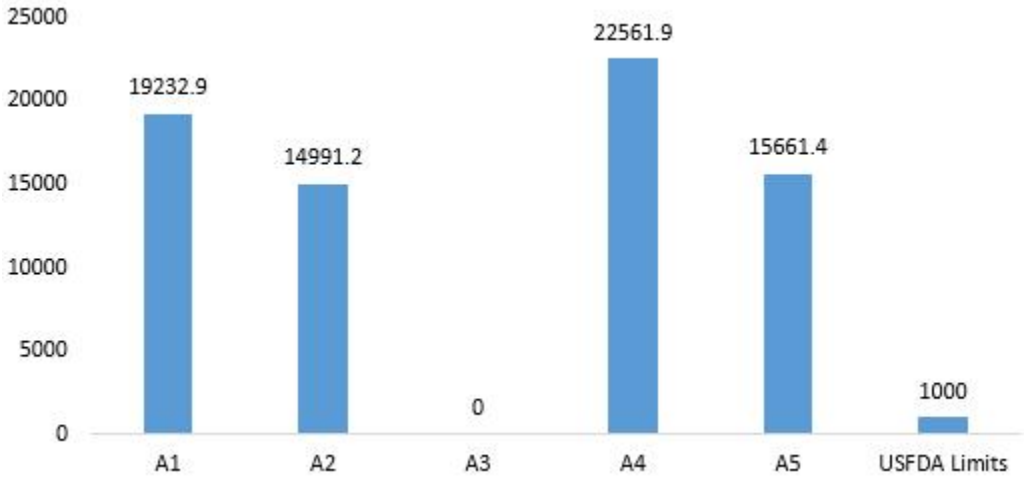

Figure 4.9: Level of Cesium in different type of hair dyes
Source: Author's Analysis, 2024

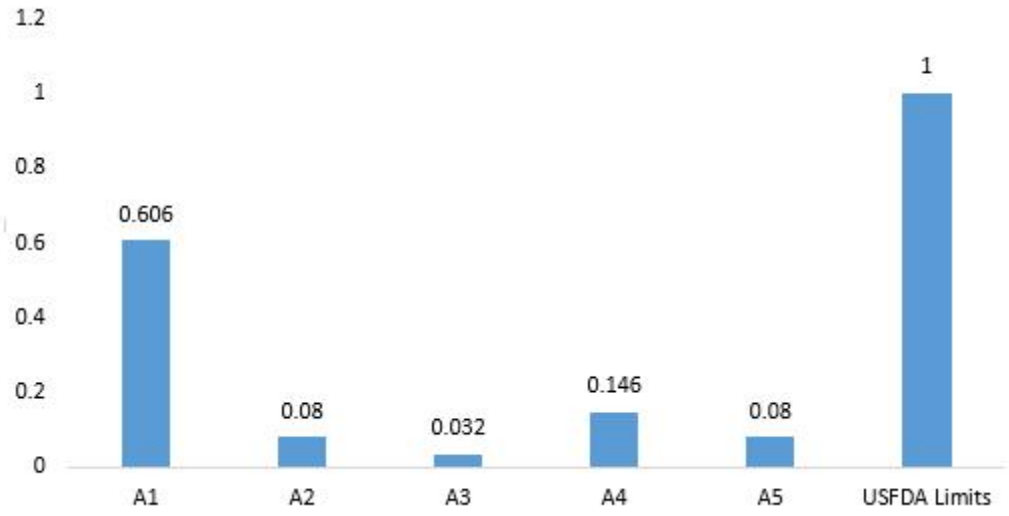

Figure 4.10: Level of Copper in different type of hair dyes
Source: Author's Analysis, 2024

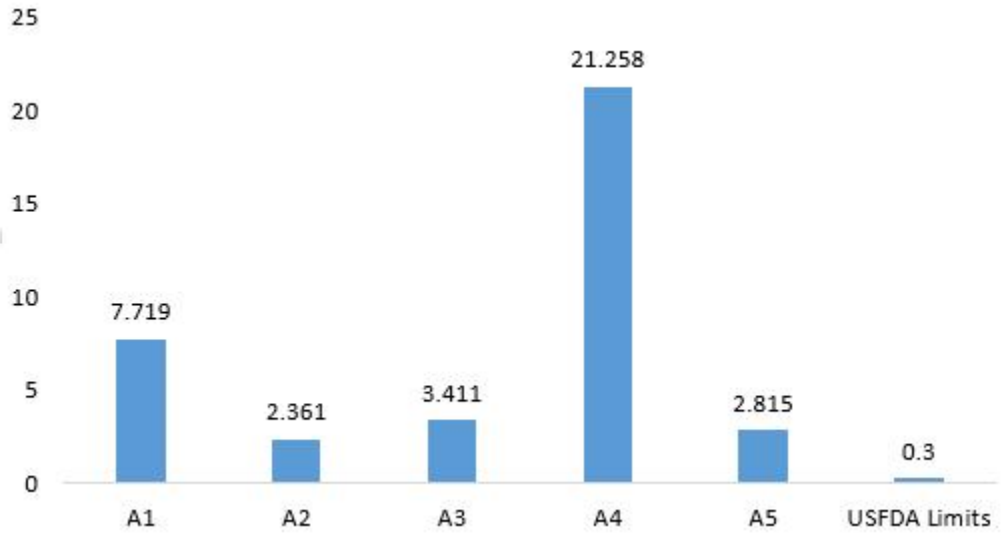

Figure 4.11: Level of Iron in different type of hair dyes
Source: Author's Analysis, 2024

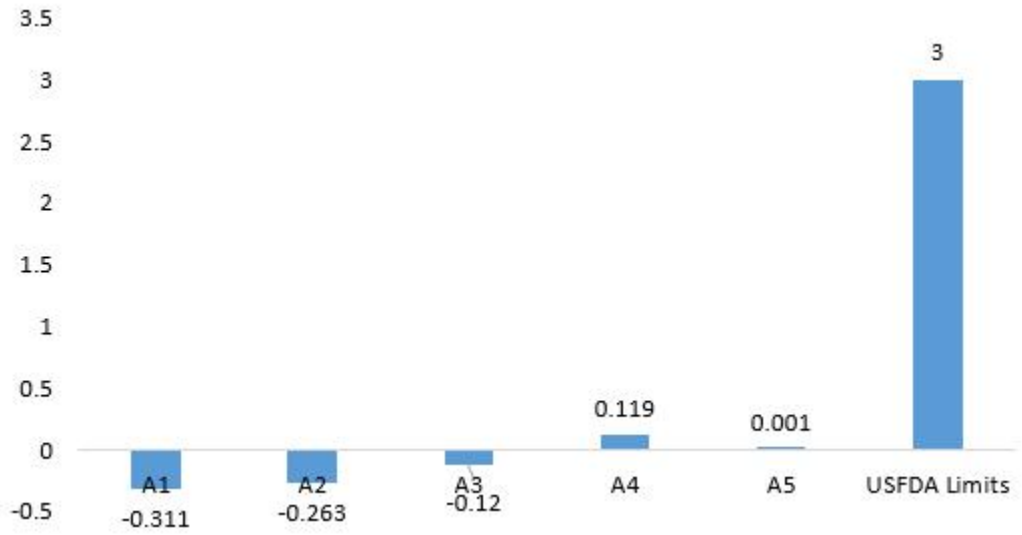

Figure 4.12: Level of Mercury in different type of hair dyes
Source: Author's Analysis, 2024

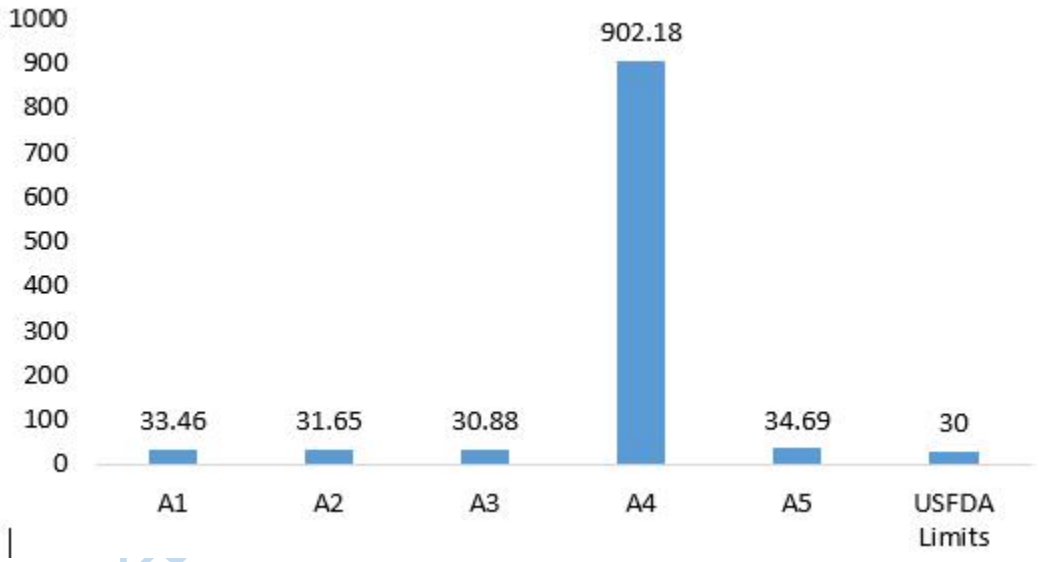

Figure 4.13: Level of Magnesium in different type of hair dyes
Source: Author's Analysis, 2024

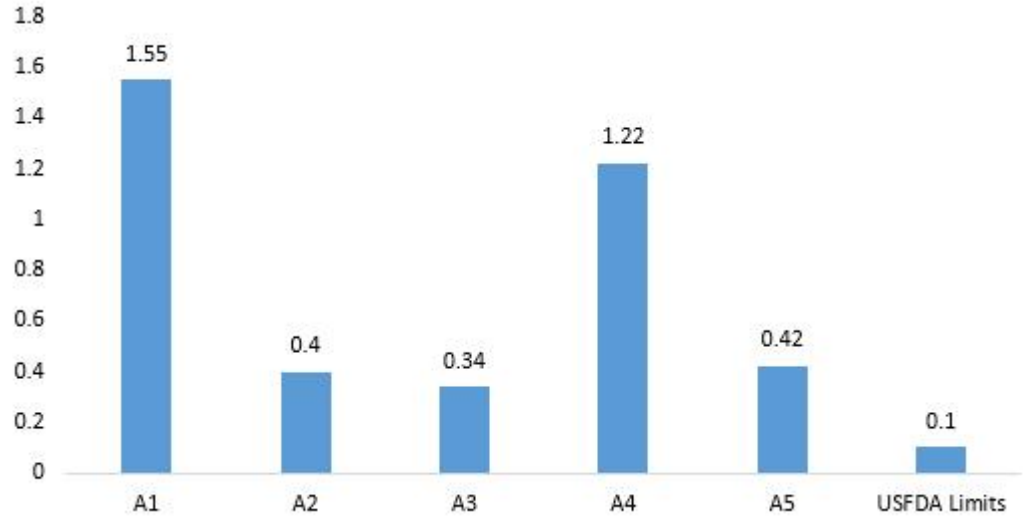

Figure 4.14: Level of Manganese in different type of hair dyes
Source: Author's Analysis, 2024

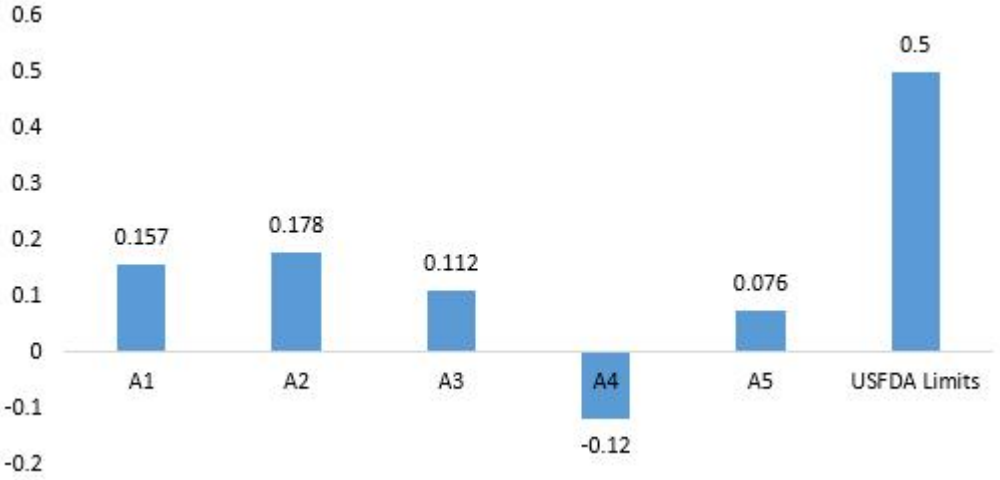

Figure 4.15: Level of Molybdenum in different type of hair dyes
Source: Author's Analysis, 2024

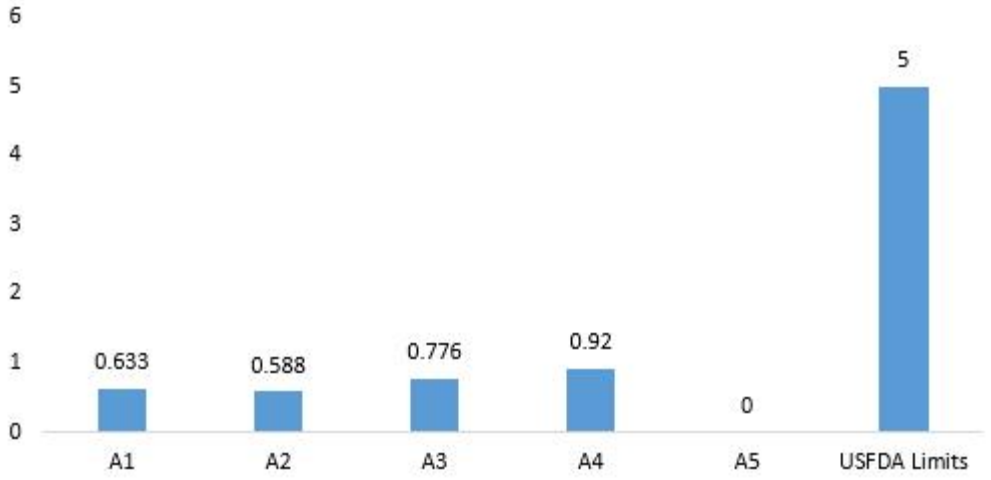

Figure 4.16: Level of Nickel in different type of hair dyes
Source: Author's Analysis, 2024

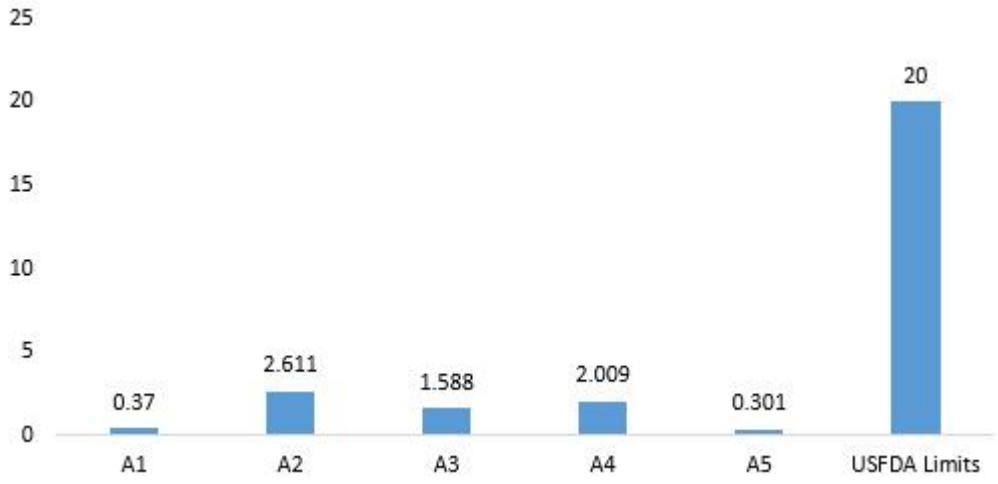

Figure 4.17: Level of Palladium in different type of hair dyes
Source: Author's Analysis, 2024

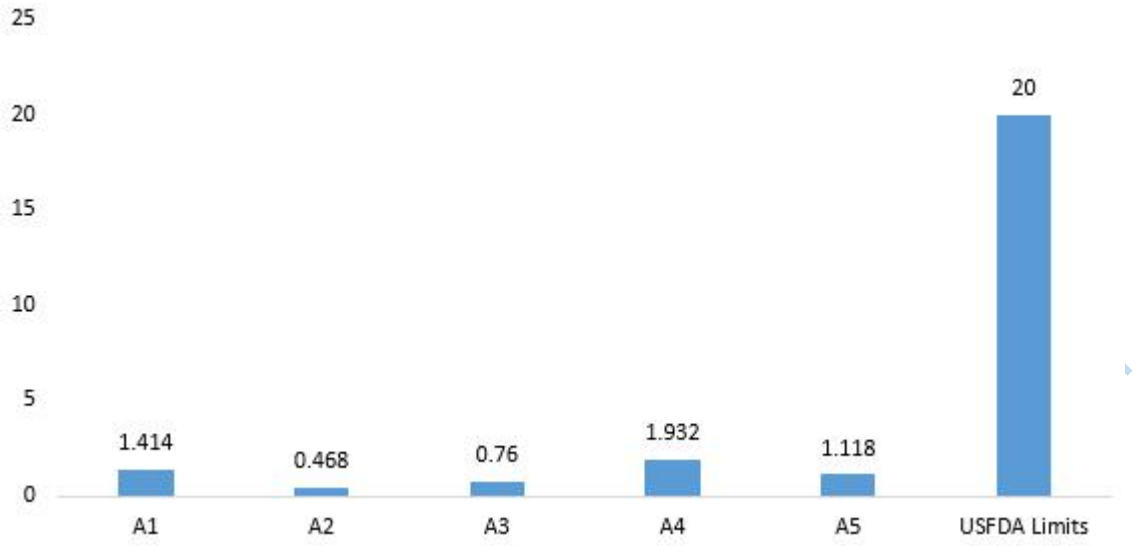

Figure 4.18: Level of Lead in different type of hair dyes
Source: Author's Analysis, 2024

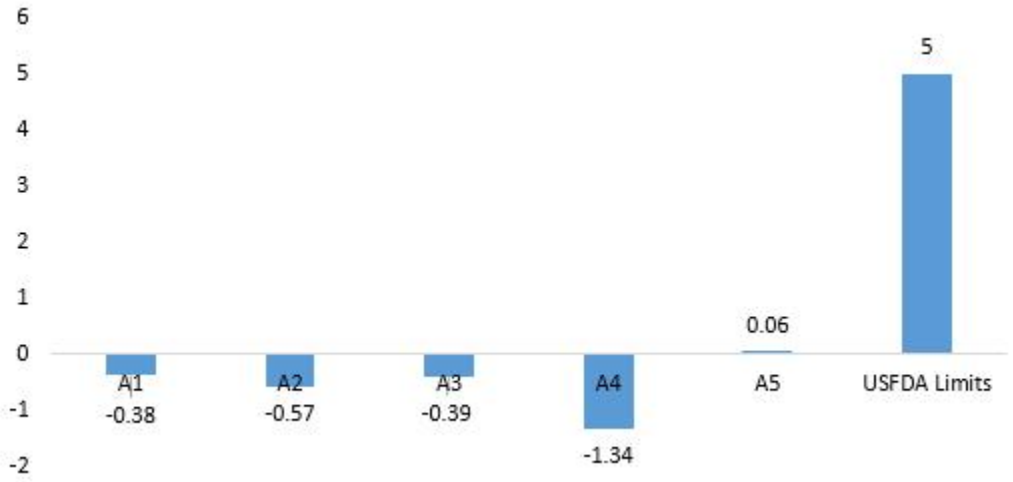

Figure 4.19: Level of Sulphur in different type of hair dyes
Source: Author's Analysis, 2024

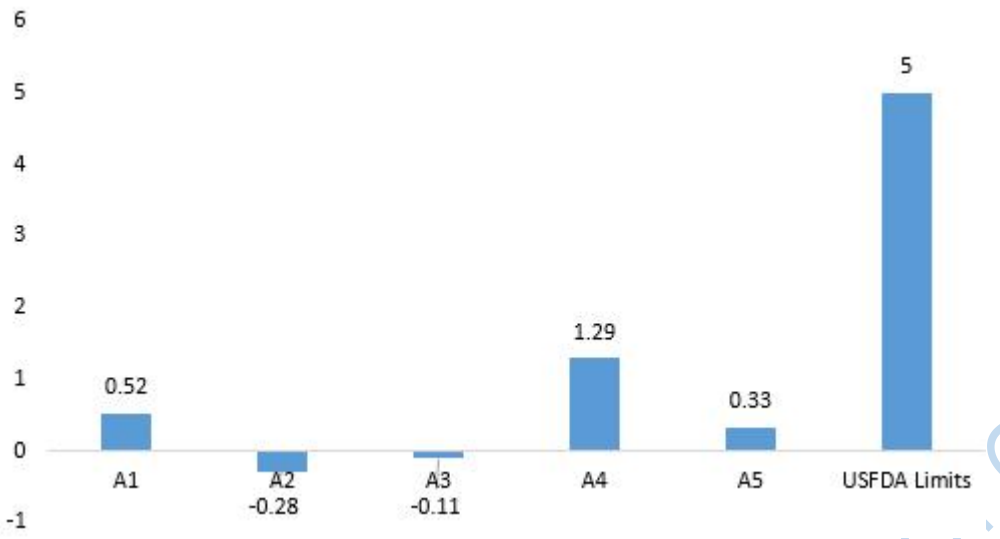

Figure 4.20: Level of Antimony in different type of hair dyes
Source: Author's Analysis, 2024

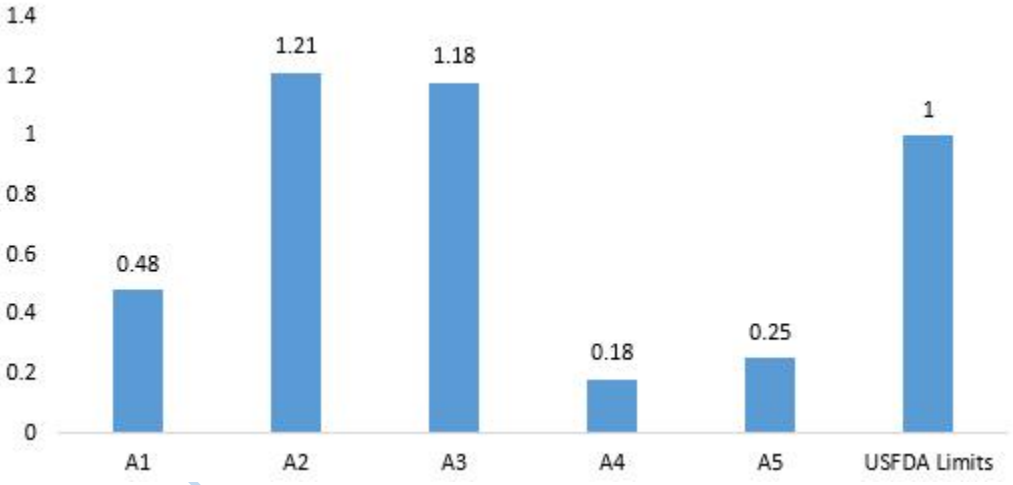

Figure 4.21: Level of Selenium in different type of hair dyes
Source: Author's Analysis, 2024

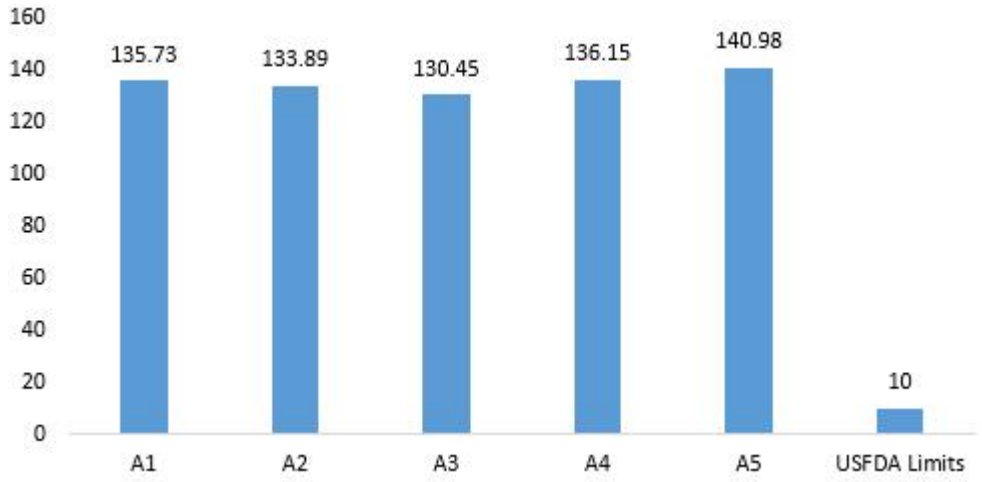

Figure 4.22: Level of Silicon in different type of hair dyes
Source: Author's Analysis, 2024

Figure 4.23: Level of Zinc in different type of hair dyes
Source: Author's Analysis, 2024

4.3 Health Risk Assessment

4.3.1 Non-carcinogenic Risk

4.3.1.1 Hazard Quotient of Ingestion (HQ_{ing}) Inhalation (HQ_{inh}) and Dermal (HQ_{derm}) Pathways and Hazard Index (HI) for the PTEs in the Hair Dye Products

The non-carcinogenic human health risk assessment for the PTEs in this investigation is summarized in Table 4.2. All of the hair dye samples had HQ_{ing} values greater than 1. All of the Pd and Si HQ_{ing} values were below allowable bounds. All of the computed HQ values for Cs and Ni were more than 1, with the exception of A3 and A5, where the value was 0.00. The risk of non-carcinogenic consequences was unacceptable for Ag, B, Cd, Cr, Fe, Mg, Ni, S, Se, and Zn in adults. Headache, diarrhea, nausea, and vomiting have all been related to elevated levels of Cr and Ni in the body[8,16].

Adults who have high amounts of Ag, Cd, Fe, Mg, Ni, B, Se, and Zn may experience health issues such memory loss, diminished attentiveness, and mental and physical retardation. With Ag, B, Cr, Mg, Ni, S, Pb, and Se as the main pollutants, the cumulative HI was computed and all values were greater than 1. This showed that using hair dye products included unacceptable risks of non-carcinogenic health impacts[4]. The non-carcinogenic HQ_{inh} in adults for the PTEs in this investigation is compiled in Table 4.3. All Ag, B, Ce, Cs, Mg, Mo, Pd, and Si had HQ_{inh} values less than 1, indicating a reasonable risk of a non-carcinogenic effect on adult human health. Since elevated levels of these PTEs in the body have been connected to headache, diarrhea, nausea, and vomiting, the HQ_{inh} values for Cd, Co, Cr, Fe, Hg, Mn, Pb, S, Sb, and Zn were all greater than 1, indicating an intolerable risk[8]. With Cd, Co, Fe, Hg, Sb, and Zn as the main pollutants, the cumulative HI was computed and all values were greater than 1. This showed that using hair dye products carried intolerable risks of non-carcinogenic health consequences[11].

The hazard quotient via dermal contact (HQ_{derm}) computation is the next stage in assessing the dangers to human health posed by PTEs in hair dye products. The results are shown in Table 4.4. There was no discernible health risk from the examined PTEs, and the computed HQ_{derm} for all Ag, Ce, Cs, Fe, Mg, Mn, Mo, Pd, and Si for various colors and brands was less than 1. Since elevated levels of certain PTEs in the body have been connected to headache, diarrhea, nausea, and vomiting, the HQ_{derm} values for B, Cd, Co, Cr, Cu, Hg, Ni, Pb, S, Sb, Se, and Zn were all greater than 1, indicating an intolerable danger. Furthermore, HI was computed using the obtained HQs in accordance with Equation 3.4; like HQ, a risk level will be significant when HI is greater than 1. The calculated HQ and HI had a non-significant interval to the baseline of 1, indicating that human exposure to these elements can have any negative effect. The calculated HI indices for the surveyed colors and brands were greater than 1, indicating that, when taking into account the overall health risk of all surveyed PTEs, using different colors and brands of chemical hair dyes is not safe[8].

Table 4.2: Hazard Quotient of Ingestion (HQ_{ing}) Pathways for the PTEs in Hair Dye for Adults

PTEs	A1	A2	A3	A4	A5
Ag	**7.82×10^{-10}**	**6.13×10^{-10}**	**5.58×10^{-11}**	**5.91×10^{-10}**	**5.85×10^{-10}**
As	**2.73×10^{-11}**	**2.19×10^{-11}**	**2.64×10^{-11}**	**2.37×10^{-11}**	**5.84×10^{-11}**
B	**6.84×10^{-11}**	1.09×10^{-11}	**7.93×10^{-10}**	**9.03×10^{-11}**	**4.92×10^{-11}**
Ce	**2.79×10^{-11}**	**2.73×10^{-11}**	**2.46×10^{-11}**	1.09×10^{-11}	**3.83×10^{-11}**
Cd	**5.47×10^{-10}**	1.36×10^{-10}	1.36×10^{-10}	1.09×10^{-10}	**8.21×10^{-10}**
Co	**8.21×10^{-11}**	**5.47×10^{-9}**	1.50×10^{-11}	**3.58×10^{-11}**	1.09×10^{-10}
Cr	**4.56×10^{-12}**	1.68×10^{-11}	**6.99×10^{-11}**	**2.90×10^{-12}**	1.84×10^{-12}
Cs	**2.63×10^{-11}**	**2.05×10^{-16}**	0.00	**3.08×10^{-16}**	**2.14×10^{-16}**
Cu	**3.31×10^{-12}**	**4.38×10^{-10}**	1.75×10^{-11}	**7.99×10^{-11}**	**4.38×10^{-12}**
Fe	**4.69×10^{-11}**	1.43×10^{-10}	**2.07×10^{-11}**	1.29×10^{-11}	1.71×10^{-11}
Hg	**2.83×10^{-11}**	**2.39×10^{-12}**	1.09×10^{-12}	1.08×10^{-12}	**9.12×10^{-12}**
Mg	**9.15×10^{-10}**	**8.60×10^{-10}**	**8.45×10^{-10}**	**2.46×10^{-12}**	**9.49×10^{-12}**
Mn	**3.03×10^{-11}**	**7.82×10^{-10}**	**6.64×10^{-10}**	**2.38×10^{-12}**	**8.21×10^{-12}**
Mo	**2.14×10^{-11}**	**2.43×10^{-10}**	1.53×10^{-11}	1.64×10^{-11}	1.04×10^{-12}
Ni	**8.6×10^{-11}**	**8.04×10^{-11}**	1.06×10^{-12}	1.25×10^{-12}	0.00
Pd	0.00	0.00	0 .00	0.00	0.00
Pb	1.10×10^{-11}	**3.66×10^{-11}**	**5.94×10^{-11}**	**1.51×10^{-11}**	**8.74×10^{-11}**
S	**5.20×10^{-11}**	**7.80×10^{-10}**	**5.33×10^{-11}**	**1.83×10^{-12}**	**8.21×10^{-12}**
Sb	**3.55×10^{-11}**	1.91×10^{-11}	**7.52×10^{-11}**	**8.82×10^{-11}**	**2.25×10^{-11}**
Se	**2.62×10^{-12}**	**6.62×10^{-12}**	**6.46×10^{-12}**	**9.85×10^{-12}**	1.30×10^{-12}
Si	0.00	0.00	0.00	0.00	0.00
Zn	**4.93×10^{-12}**	**7.20×10^{-12}**	1.02×10^{-12}	1.13×10^{-12}	**5.56×10^{-12}**
HI	**2.63×10^{-16}**	**2.05×10^{-16}**	**3.08×10^{-16}**	**2.14×10^{-16}**	**1.89×10^{-12}**

Bold figures indicate values greater than 1.

Source: Author's Analysis, 2024

Table 4.3: Hazard Quotient of Inhalation (HQ_{inh}) Pathways for the PTEs in Hair Dyes for Adults

PTEs	A1	A2	A3	A4	A5
Ag	0.00	0.00	0.00	0.00	0.00
As	1.64 $\times 10^{-11}$	1.31 $\times 10^{-11}$	1.58 $\times 10^{-11}$	1.42 $\times 10^{-11}$	**3.50 $\times 10^{-11}$**
B	0.00	0.00	0.00	0.00	0.00
Ce	0.00	0.00	0.00	0.00	0.00
Cd	**2.73 $\times 10^{-11}$**	**6.84 $\times 10^{-11}$**	**6.84 $\times 10^{-11}$**	**5.47 $\times 10^{-11}$**	**4.10 $\times 10^{-11}$**
Co	**8.21 $\times 10^{-10}$**	**5.47 $\times 10^{-10}$**	1.50 $\times 10^{-10}$	**3.55 $\times 10^{-11}$**	1.09 $\times 10^{-11}$
Cr	**9.12 $\times 10^{-10}$**	**3.37 $\times 10^{-10}$**	1.39 $\times 10^{-10}$	**5.80 $\times 10^{-10}$**	**3.68 $\times 10^{-10}$**
Cs	0.00	0.00	0.00	0.00	0.00
Cu	**3.31 $\times 10^{-11}$**	**4.38 $\times 10^{-11}$**	**4.38 $\times 10^{-11}$**	**7.99 $\times 10^{-11}$**	**4.38 $\times 10^{-11}$**
Fe	**8.45 $\times 10^{-11}$**	**2.58 $\times 10^{-11}$**	**3.73 $\times 10^{-11}$**	**2.32 $\times 10^{-11}$**	**3.08 $\times 10^{-11}$**
Hg	**5.67 $\times 10^{-11}$**	**4.79$\times 10^{-11}$**	**2.19 $\times 10^{-11}$**	**2.17 $\times 10^{-11}$**	1.82 $\times 10^{-11}$
Mg	0.00	0.00	0.00	0.00	0.00
Mn	**4.24 $\times 10^{-11}$**	1.09 $\times 10^{-11}$	**9.30 $\times 10^{-11}$**	**3.33 $\times 10^{-11}$**	1.14 $\times 10^{-11}$
Mo	0.00	0.00	0.00	0.00	0.00
Ni	1.73 $\times 10^{-11}$	1.60 $\times 10^{-11}$	**2.12 $\times 10^{-11}$**	**2.51 $\times 10^{-11}$**	0.00
Pd	0.00	0.00	0.00	0.00	0.00
Pb	1.54 $\times 10^{-11}$	**5.12 $\times 10^{-11}$**	**8.32 $\times 10^{-11}$**	**2.11 $\times 10^{-11}$**	1.22 $\times 10^{-11}$
S	**2.08 $\times 10^{-11}$**	**3.12 $\times 10^{-11}$**	**2.13 $\times 10^{-11}$**	**7.33 $\times 10^{-11}$**	**3.28 $\times 10^{-11}$**
Sb	**7.11 $\times 10^{-11}$**	**3.83 $\times 10^{-11}$**	1.50 $\times 10^{-11}$	1.76 $\times 10^{-11}$	**4.51 $\times 10^{-11}$**
Se	**5.25 $\times 10^{-11}$**	1.32 $\times 10^{-11}$	1.29 $\times 10^{-11}$	1.97 $\times 10^{-11}$	**2.62 $\times 10^{-11}$**
Si	0.00	0.00	0.00	0.00	0.00
Zn	**2.04 $\times 10^{-11}$**	**8.65 $\times 10^{-11}$**	1.22 $\times 10^{-11}$	1.35 $\times 10^{-11}$	**6.67 $\times 10^{-11}$**
HI	1.11 $\times 10^{-11}$	**6.35 $\times 10^{-11}$**	1.24 $\times 10^{-11}$	**6.96 $\times 10^{-11}$**	**7.01 $\times 10^{-11}$**

Bold figures indicate values greater than 1.

Source: Author's Analysis, 2024

Table 4.4: Hazard Quotient of Dermal (HQ_{derm}) Pathways for the PTEs in Hair Dyes for Adults

PTEs	A1	A2	A3	A4	A5
Ag	0.00	0.00	0.00	0.00	0.00
As	1.36×10^{-11}	1.09×10^{-11}	1.32×10^{-11}	1.18×10^{-11}	**2.92×10^{-11}**
B	**3.42×10^{-11}**	**5.47×10^{-10}**	**3.96×10^{-10}**	**4.51×10^{-10}**	**2.46×10^{-10}**
Ce	0.00	0.00	0.00	0.00	0.00
Cd	**2.73×10^{-10}**	**6.84×10^{-10}**	**6.84×10^{-10}**	**5.47×10^{-10}**	**4.10×10^{-10}**
Co	**4.10×10^{-11}**	**2.73×10^{-11}**	**7.52×10^{-11}**	1.77×10^{-11}	**5.47×10^{-11}**
Cr	**2.28×10^{-11}**	**8.44×10^{-11}**	**3.49×10^{-11}**	1.45×10^{-11}	**9.21×10^{-11}**
Cs	0.00	0.00	0.00	0.00	0.00
Cu	1.65×10^{-10}	**2.19×10^{-10}**	**8.76×10^{-10}**	**3.99×10^{-10}**	**2.19×10^{-10}**
Fe	0.00	0.00	0.00	0.00	0.00
Hg	**4.25×10^{-11}**	**3.59×10^{-11}**	1.64×10^{-11}	1.62×10^{-11}	1.36×10^{-11}
Mg	0.00	0.00	0.00	0.00	0.00
Mn	0.00	0.00	0.00	0.00	0.00
Mo	0.00	0.00	0.00	0.00	0.00
Ni	**4.33×10^{-11}**	**4.02×10^{-11}**	**5.31×10^{-11}**	**6.29×10^{-11}**	0.00
Pd	0.00	0.00	0.00	0.00	0.00
Pb	**4.83×10^{-11}**	1.60×10^{-11}	**2.60×10^{-11}**	**6.61×10^{-11}**	**3.82×10^{-11}**
S	**2.60×10^{-11}**	**3.90×10^{-10}**	**2.66×10^{-10}**	**9.17×10^{-10}**	**4.10×10^{-10}**
Sb	1.77×10^{-11}	**9.58×10^{-11}**	**3.76×10^{-11}**	**4.41×10^{-11}**	1.12×10^{-11}
Se	1.31×10^{-11}	**3.31×10^{-11}**	**3.23×10^{-11}**	**4.92×10^{-11}**	**6.57×10^{-11}**
Si	0.00	0.00	0.00	0.00	0.00
Zn	**5.11×10^{-11}**	**2.16×10^{-11}**	**3.06×10^{-11}**	**3.39×10^{-11}**	1.66×10^{-11}
HI	1.69×10^{-11}	1.18×10^{-11}	**2.04×10^{-11}**	**8.13×10^{-11}**	1.20×10^{-11}

Bold figures indicate values greater than 1.

Source: Author's Analysis, 2024

4.4 Lifetime Cancer Risk (LCR) for PTEs through Ingestion, Inhalation and Dermal Pathways

The International Agency for Research on Cancer lists As, Cr, Co, Pb, and Ni as carcinogenic PTEs[9]. Table 4.5, 4.6 and 4.7 summarizes the estimated lifetime cancer risk (LCR) values for the metals (As, Cd, Cr, Co, Pb, and Ni) found in this investigation. PTEs can enter the body in three main ways: through the skin, through ingestion, or through inhalation. PTEs build in the body for a long time since they are not biodegradable. Consequently, they affect intracellular pathways in addition to changing how cells function[6]. Consequently, contaminants that lead to oxidative stress, DNA damage, and cell death exacerbate disorders associated with cancer[8]. The calculation of the possible cancer risk to users resulting from exposure to PTEs from hair dye products is known as lifetime cancer risk, or LCR. The USEPA states that the permissible range for LCR is between 1×10^{-6} and 1×10^{-4} [2,3].

According to Table 4.5, the LCR values of PTEs obtained from ingestion ranged from 0.00 to 21.1×10^{-9}. They were found to be in decreasing order of As > Cr > Cd > Pb > Ni > Co. A few of these values exceeded the 1.0×10^{-6} to 1.0×10^{-4} safe range that the USEPA recommends [2]. With the exception of Ni in A5, the projected cancer risk for As, Cr, Cd, and Pb was higher than the permissible levels. All of the Co values were zero. A3 (gold) has the lowest cancer risk by ingestion, while A1 (black) is the most carcinogenic of the hair dyes examined based on cumulative lifetime cancer risk (LCR). Furthermore, all six PTEs had estimated LCR values above the allowable limit of 1.0×10^{-4}, with the exception of Co, which suggested a carcinogenic risk for those who consumed these hair dyes[8]. The LCR values of PTEs obtained by inhalation are shown in Table 4.6. They were all over the permissible limits, with the exception of Ni in A5, and were discovered in the following decreasing order: Cr > Co > As > Ni > Cd > Pb. All of the

Pb levels were 0.00. A2 has the lowest cancer risk through inhalation, while A4 is the most carcinogenic of the hair dyes examined based on cumulative lifetime cancer risk (LCR). Furthermore, all six PTEs had projected LCR values above the allowable limits of 1.0×10^{-4}, with the exception of Pb, suggesting that inhaling these hair dyes could cause cancer[8].

The cumulative LCR of dermal values obtained, present in Table 4.6 gave values of 11.3×10^{-5}, 9×10^{-5}, 7.1×10^{-7}, 16.4×10^{-5} and 20×10^{-4}, respectively, for A1, A2, A3, A4 and A5. Therefore, the values of LCR dermal of PTEs analyzed for adults were found in the order of A5 > A4 > A1 > A2 > A3. Mean values of 8.7×10^{-4}, 17.6×10^{-5}, 22.8×10^{-5}, 0.00, 0.00 and 14.7×10^{-5} respectively, were observed for As, Cd, Cr, Ni, Co, and Pb. As a result, the LCR dermal values of PTEs examined for adults were found to be in the following order: Cr > Cd > Pb > As > Ni > Co.

The lifetime cancer risk was found to be higher than the allowable limits for all of the PTEs that were examined, with the exception of Ni and Co, indicating that hair dye products may have a lifetime cancer risk. Because this value is below the threshold at which cancer risk is deemed problematic, the LCR of Ni and Co may therefore be regarded as negligible and the cancer risk can be disregarded. Because of their cutaneous sensitivity to Cr, Cd, Pb, and As, the hair dye samples examined in this investigation did, in fact, provide a carcinogenic risk.

Table 4.5: Lifetime Cancer Risk (LCR) for PTEs through Ingestion Pathways

	As	Cd	Cr	Ni	Co	Pb	ΣLCR
A1 (black)	**1.2×10^{-9}**	**8.2×10^{-9}**	**6.8×10^{-9}**	**1.6×10^{-9}**	0.00	**3.3×10^{-9}**	**21.1×10^{-9}**
A2 (green)	**9.9×10^{-7}**	**2.1×10^{-7}**	**2.5×10^{-7}**	**1.5×10^{-7}**	0.00	**1.1×10^{-7}**	**17.1×10^{-7}**
A3 (gold)	**1.2×10^{-8}**	**2.1×10^{-8}**	**1.0×10^{-8}**	**1.9×10^{-8}**	0.00	**1.8×10^{-8}**	**8×10^{-8}**
A4 (white)	**1.1×10^{-8}**	**1.6×10^{-8}**	**4.4×10^{-8}**	**2.3×10^{-8}**	0.00	**4.5×10^{-8}**	**13.9×10^{-8}**
A5 (wine)	**2.6×10^{-9}**	**1.2×10^{-9}**	**2.8×10^{-9}**	0.00	0.00	**2.6×10^{-9}**	**9.2×10^{-9}**

Bold figures for LCR indicate values >1.0 x 10^{-6}, ΣLCR = cumulative cancer risk.

Source: Author's Analysis, 2024

Table 4.6: Lifetime Cancer Risk (LCR) for PTEs through Inhalation Pathways

	As	Cd	Cr	Ni	Co	Pb	ΣLCR
A1	**2.5×10^{-6}**	**6.9×10^{-6}**	**1.1×10^{-6}**	**2.9×10^{-6}**	**1.6×10^{-6}**	0.00	**15×10^{-6}**
A2	**2.0×10^{-8}**	**1.7×10^{-8}**	**4.3×10^{-8}**	**2.7×10^{-8}**	**1.1×10^{-8}**	0.00	**11.8×10^{-8}**
A3	**2.4×10^{-7}**	**1.7×10^{-7}**	**1.8×10^{-7}**	**3.6×10^{-7}**	**3.0×10^{-7}**	0.00	**12.5×10^{-7}**
A4	**2.1×10^{-7}**	**1.4×10^{-7}**	**7.3×10^{-7}**	**4.2×10^{-7}**	**7.0×10^{-7}**	0.00	**21×10^{-7}**
A5	**5.3×10^{-9}**	**1.0×10^{-9}**	**4.6×10^{-9}**	0.00	**2.1×10^{-9}**	0.00	**13×10^{-9}**

Bold figures for LCR indicate values > 1.0×10^{-6}, ΣLCR = cumulative cancer risk.

Source: Author's Analysis, 2024

Table 4.7: Lifetime Cancer Risk (LCR) for PTEs through Dermal Pathways

	As	Cd	Cr	Ni	Co	Pb	ΣLCR
A1	**1.5×10^{-4}**	**5.5×10^{-4}**	**1.4×10^{-4}**	0.00	0.00	**2.9×10^{-4}**	**11.3×10^{-5}**
A2	**1.2×10^{-5}**	**1.4×10^{-5}**	**5.1×10^{-5}**	0.00	0.00	**1.3×10^{-5}**	**9×10^{-5}**
A3	**1.5×10^{-7}**	**1.4×10^{-7}**	**2.1×10^{-7}**	0.00	0.00	**2.1×10^{-7}**	**7.1×10^{-7}**
A4	**1.3×10^{-5}**	**1.1×10^{-5}**	**8.7×10^{-5}**	0.00	0.00	**5.3×10^{-5}**	**16.4×10^{-5}**
A5	**3.2×10^{-4}**	**8.2×10^{-4}**	**5.5×10^{-4}**	0.00	0.00	**3.1×10^{-4}**	**20×10^{-4}**

Bold figures for LCR indicate values >1.0 x 10^{-6}, ΣLCR = cumulative cancer risk

Source: Author's Analysis, 2024

Endnotes

1. *C.D.C. Center for Disease Control and Prevention. Low level lead exposure harms children: a renewed call for primary prevention. In report of the advisory committee on childhood lead poisoning prevention; CDC: Atlanta, GA, USA,* 2012.

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Chapter Five

Conclusion

5.1 Summary of Findings

In the present study; Ag, As, B, Ce, Cd, Co, Cr, Cs, Cu, Fe, Hg, Mg, Mn, Mo, Ni, Pd, Pb, S, Sb, Se, Si and Zn were determined in different brands of hair dyes using ICP-OES. Carcinogenic, non-carcinogenic, ingestion, inhalation, and dermal sensitivity health risk assessments related to consuming these products were also studied. The studied PTEs concentrations were ranged as; Cs > Mg > Si > Fe > Pd > Pb > Ag > Zn > Mn > Se > Ni > Ce > Sb > As > Cr > B > Cu > Mo > Co > Cd > S > Hg respectively across all hair dye products. The concentration values for Ag, Ce, Cs, Fe, Mg, Mn, and Si were all below the USFDA permissible limit. The concentration values of As, B, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pd, Pb, S, and Zn were observed to be higher than the permissible limits in all the samples except for Se in A1, A4 and A5 with values of 0.48, 0.18 and 0.25 respectively.

The HQ_{ing} for all the hair dye samples was all greater than 1. The HQ_{ing} values for Pd and Si were all below acceptable limits. For Cs and Ni, all the calculated HQ values were > 1 except for A3 and A5 with a value of 0.00 apiece. Ag, B, Cd, Cr, Fe, Mg, Ni, S, Se and Zn showed unacceptable risks of non-carcinogenic effects in adults. The cumulative HI was calculated and all values were > 1 across all sampling sites with Ag, B, Cr, Mg, Ni, S, Pb, and Se as the dominant contaminants. The HQ_{inh} for all Ag, B, Ce, Cs, Mg, Mo, Pd, and Si were all < 1 which indicated an acceptable risk of a non-carcinogenic effect on human health in adults. The cumulative HI was calculated and all values were > 1 across all hair dyes with Cd, Co, Cd, Fe, Hg, Sb, and Zn as the dominant contaminants. The calculated HQ_{derm} for all Ag, Ce, Cs, Fe, Mg, Mn, Mo, Pd, and Si for different colors and brands were < 1, and there was no significant health

risk from investigated PTEs. The calculated HQ and HI had a non-significant interval to the baseline of 1, indicating that human exposure to these elements can have any negative effect. The calculated HI indices for the surveyed colors and brands were greater than 1, indicating that, when taking into account the overall health risk of all surveyed PTEs, the consumption of various white (Subaru) and black (Cruset) chemical hair dyes is not safe.

The LCR values of PTEs through ingestion were found to be in decreasing order of As > Cr > Cd > Pb > Ni > Co and the values ranged from to 0.00 to 21.1×10^{-9}. Some of these values were above the USEPA recommended safe range of 1.0×10^{-6} to 1.0×10^{-4}. Pb values were all 0.00. The values of LCR dermal of PTEs analyzed for adults were found in the order of A5 > A4 > A1 > A2 > A3. Mean values of 8.7×10^{-4}, 17.6×10^{-5}, 22.8×10^{-5}, 0.00, 0.00 and 14.7×10^{-5} respectively, for As, Cd, Cr, Ni, Co, and Pb. As a result, the LCR dermal values of PTEs examined for adults were found to be in the following order: Cr > Cd > Pb > As > Ni > Co. With the exception of Ni and Co, all of the examined PTEs had lifetime cancer risks that were predicted to be higher than the allowable level, suggesting that the hair color products may have a lifelong cancer risk.

5.2 Conclusion

An assessment of the health concerns associated with PTE exposure in the most popular hair dye products in Ibadan, Nigeria, revealed that they were present in the tested goods, albeit in subpar quality compared to the USFDA's requirements. Customers using these hair dyes in Ibadan, Nigeria, are anticipated to face clear carcinogenic and non-carcinogenic dangers, based on the data obtained. The LCR presents a danger of cancer with repeated and prolonged use of these hair dyes through hand-dermal contact, ingestion, and inhalation, which can result in long-term health issues for users. This risk applies to all investigated PTEs. Regular use of these hair dyes

may cause an unnecessary accumulation of PTEs in the body, which could have negative effects on both humans and other animals.

5.3 Recommendations

Based on the outcome of this study, the following are hereby recommended:

1. Long term (2 – 3 years) use of hair dyes should be discouraged, especially for people with cancer family history.
2. To better protect the health of customers, consumer protection agencies must regularly regulate the amounts of PTEs in hair dye products sold in Nigerian supermarkets.

5.4 Contribution to Knowledge

The findings from this study could be utilized for further research because information on PTEs levels in hair dyes are scarce. This study has provided a new set of data on presence of PTEs in hair dyes.

5.5 Suggested Areas for Further Research

1. Further study on organic components such as; parabens and total hydrocarbon contents of the hair dye products is highly suggested, using appropriate analytical tools. Energy.
2. Dispersive X-ray spectroscopy (EDX) in hair dyes should be studied further to unveil and display the elemental match-up with the dye colors.

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Hair Dye Use Questionnaire

Section 1: Demographics

1. Age Group:

☐ Under 18

☐ 18–25

☐ 26–35

☐ 36–45

☐ 46–55

☐ 56 and above

2. Gender:

☐ Male

☐ Female

3. Location: (City/Region)

_____

4. Occupation:

_____

Section 2: Hair Dye Usage

5. Have you ever used hair dye?

☐ Yes

☐ No

6. If yes, for long?

☐ Once a month or more

☐ Every 2–3 months

☐ 2–3 years

☐ Once or twice a year

☐ Rarely (less than once a year)

7. What is your primary reason for using hair dye?

☐ Covering gray/white hair

☐ Experimenting with new colors/styles

☐ Enhancing natural hair color

☐ Fashion or personal expression

☐ Other (please specify): _____

8. What type of hair dye do you typically use?

☐ Permanent

☐ Semi-permanent

☐ Temporary

☐ Henna or natural dyes

☐ Other: _____

9. Where do you typically apply hair dye?

☐ At home

☐ At a salon

☐ Other (please specify): _____

Section 3: Product Preferences

10. Which factors influence your choice of hair dye? (Select all that apply):

☐ Brand reputation

☐ Price

☐ Availability

☐ Ingredients (e.g., natural/chemical-free)

☐ Range of colors

☐ Durability/longevity

☐ Recommendations from friends/family

☐ Online reviews

☐ Other: _____

11. Do you prefer a specific brand or product?

☐ Yes (please specify): _____

☐ No preference

Section 4: Experiences & Concerns

12. Have you experienced any side effects from using hair dye?

☐ No

☐ Yes (please specify): _____

13. How satisfied are you with your hair dye experience?

☐ Very satisfied

☐ Somewhat satisfied

☐ Neutral

☐ Somewhat dissatisfied

☐ Very dissatisfied

14. What concerns do you have regarding hair dye? (Select all that apply):

☐ Hair damage

☐ Skin allergies/irritation

☐ Environmental impact

☐ Health risks (e.g., chemical exposure)

☐ Cost

☐ Other: _____

Section 5: Feedback & Suggestions

15. What improvements would you like to see in hair dye products?

_____

16. Would you recommend hair dye to others?

☐ Yes

☐ No

☐ It depends (please specify): _____

17. Additional Comments or Suggestions:

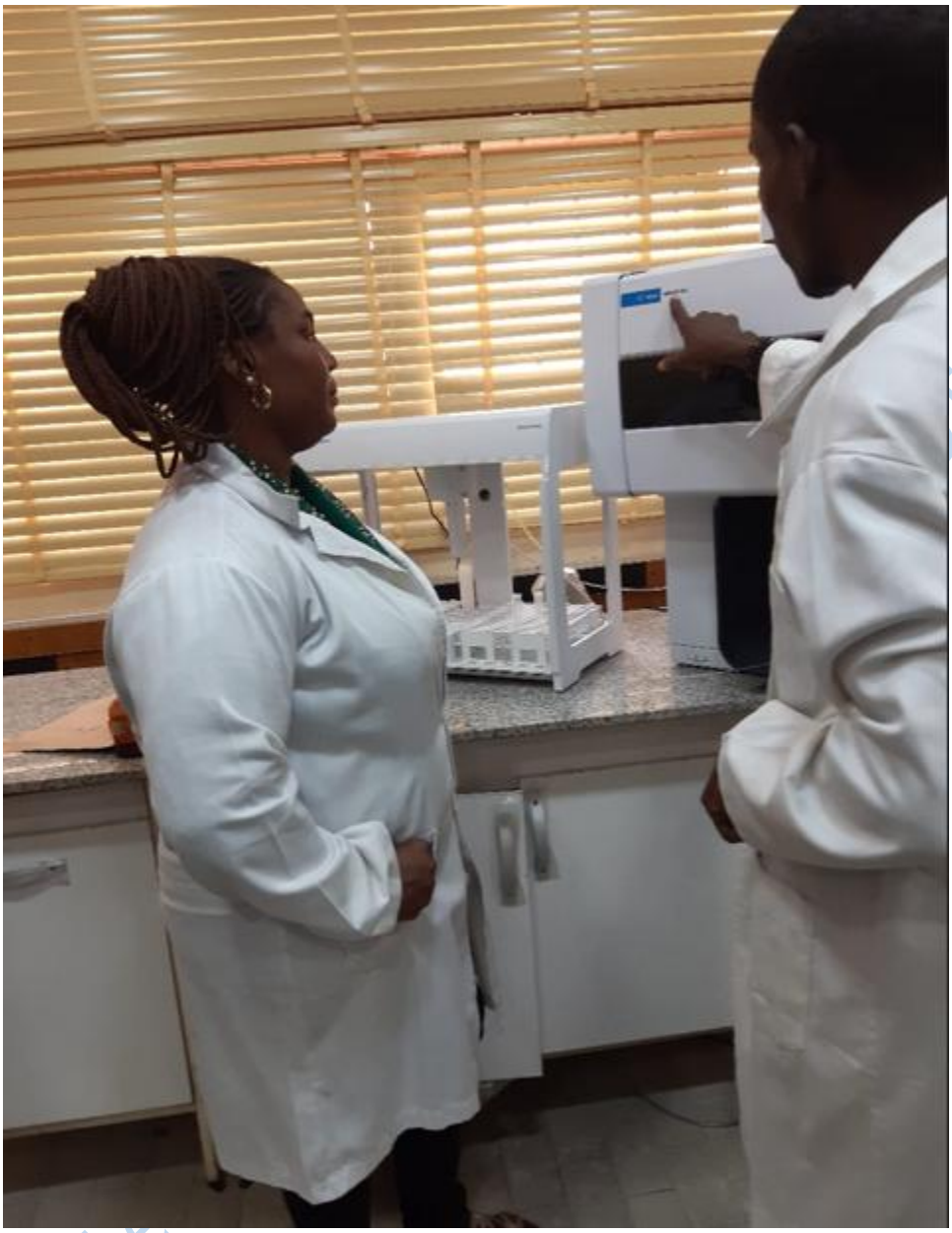
_____

This questionnaire aims to collect detailed data about users' behaviors, preferences, and concerns regarding hair dye usage.

Appendix 1: Different types of Hair Dyes Used in the Study

Appendix II: ICP-OES Instrumentation

Appendix III: Conducting the Analysis on ICP-OES



Bio-data

A. Personal Data

Full Names	Sakirat Dasola, DANJUMA
Permanent Home Address	8, Flat, Oluyole Sharp Corner, Ibadan, Oyo State.
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Date of Birth	19th July, 1985
Place of Birth	Ibadan, Oyo State.
Nationality	Nigerian
Next of Kin	Danjuma Abiru, Adams
Address	8, Flat, Oluyole Sharp Corner, Ibadan, Oyo State.

B. Education Background

Educational Institutions Attended with Dates and Qualifications

- Lead City University, {MSc. Industrial Chemistry} 2022 – till date
- Lead City University, {PGD Industrial Chemistry} 2019 – 2021
- The Polytechnic Ibadan {HND in Applied Chemistry} 2007 - 2009
- The Polytechnic Ibadan, {ND in Science Lab. Tech.} 2004 - 2006
- Community High School, Akufo, Ibadan, Oyo State

  (Senior Secondary School Certificate) 1995 - 2001
- Army Children School 1, Mokola, Ogun State

  (Primary school leaving certificate) 1990 - 1995

C. Work Experience with Dates

Work Experience Outside the College

- Independent National Electoral College (INEC) 2011
- Community Secondary School (CSS) Otusega Ogbia L.G.A 2010
- Industrial Attachment Training (IT)
- Low-Cost Cosmetic and Soap Industries, Sango, Ibadan 2009

Working Experience within College

- Federal College of Animal Health & Production Technology, Moor Plantation Ibadan – Teaching Students and Project Supervision 2012 – Till date

D. Awards and Fellowship

Nil

E. Membership of Academic Professional Bodies

- Nigerian Institute of Science Laboratory Technology (NISLT)
- Admission and Orientation Committee (FCAH&PT)
- Social and Welfare Committee (FCAH&PT)
- Project Committee (FCAH&PT)

F. Publications: **Thesis and Dissertation**

- Investigation and Health Risk Assessment of Certain Potential Toxic Elements (PTEs) in Selected Hair Dye Products
- Elementary Dietary Exposure from two Medicinal Herbs Community is sold as Blood Booster in Ibadan.
- Proximate Analysis and Fatty Acid Profile of Dried Fish and Kilishi Delicacy Consumed in Southwest Nigeria.
- Phytochemical Screening of Leaves and Stembark of *Magnifera Indica*

G. References

Dr. A. G. Ibrahim
Provost
Federal Cooperative College
Ibadan, Oyo State

Mr. R. A. Salako
Director of Lab. Service
Federal College of Animal
Health & Production Technology
Ibadan, Oyo State

…… ……

Signature **Date**

The University Compliance Certification

This is to certify that this Thesis was written by **Sakirat Dasola DANJUMA with Matric Number LCU/PG/001323** of the Department of Chemical Sciences, Faculty of Natural and Applied Sciences, Lead City University, Ibadan and it is in full compliance with the approved University format and style.

……..... …….....

Signature **Date**


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