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Assessment of Some Heavy Metals in Selected Cosmetics Commonly Sold in Katsina Markets and Their Human Health Risk

Surajo I.T.[1], Haruna A.[2], Kusharki H.M.[3], Ruma M.M.[4] and Salisu A.[5]
[1]Department of Pure and Industrial Chemistry, Bayero University, Kano, NIGERIA.
[2]Department of Chemistry, Federal University, Gusau, Zamfara, NIGERIA.
[3]Department of Chemistry. Al-Qalam University, Katsina, NIGERIA.
[4]Department of Chemistry. Al-Qalam University, Katsina, NIGERIA.
[5]Department of Chemistry, Federal University, Gusau, Zamfara, NIGERIA.

[2]Corresponding Author: anasharunaabk@gmail.com

ABSTRACT

Cosmetic product protection is a serious concern because of the presence of heavy metals. Accumulation of these metals affect human body over a time. The study was aimed at assessing the levels of some toxic metals in different cosmetic products sold at different shops and markets in Katsina metropolis. The cosmetic items included nine face powder and nine lipsticks. The cosmetics were digested and analyzed for heavy metals (Ni, Cd, Cr and Pb) using Atomic Absorption Spectrophotometer. Risk of this metals to the consumer was determine using systematic exposure dosage (SED), margin of safety (MoS), hazard quotient (HQ), hazard index (HI) and cancer risk (CR). The range of the concentration in face powder was 0.007-0.624±0.003-1.508 mg/kg. The concentration ranges in lipsticks was 0.012-0.036 ± 0.009-0.036 mg/kg. Lead has the highest concentration in face powder and chromium has the highest concentration range in lipstick, while cadmiun has the least concentration in both face powders and lipsticks. The concentration of all the heavy metals are below permissible limit. The Margin of Safety (MoS) values calculated for different metals were higher than the established safe standard by WHO except for Cr in face powders. The obtained SED values are much lower than PTDI. HQ values were within permissible limit indicating low risk of detrimental effect. HI value is greater than one in face powder and less than one in lipsticks. The carcinogenic risk (CR) estimated are within permissible limit except for Cd.

Keywords- Health Risk Assessment, Heavy Metals, Cosmetic, Systemic Exposure Dosage Hazard Quotient.

I. INTRODUCTION

Cosmetics are classified as any item applied to the human body for the cleaning, beautification, attractiveness, or modification of the visual aspect that does not affect the creation or function (Alam *et al.,* 2019; Balarastaghi *et al.,* 2017). Cosmetic product protection is a serious concern and has attracted the researchers, toxicologists, and regulators; with the objective of ensuring ingredient protection (Idris *et al.,* 2019; Brandao *et al.,* 2012).Heavy metal concentrations are found naturally in rocks, soil and water and therefore are constituents of pigments and other raw materials used in the cosmetics industry. They can also be used as additives, as in the case of preservative thimerosal (mercury), the progressive hair dye lead acetate and a number of tattoo pigments such as red cinnabar (mercuric sulfide), cadmium is a deep yellow to orange pigment and mostly present in face powders (Nourmoradi *et al.,* 2013). The coloring property of cadmium (Cd) make it one of the useful agent in cosmetic products such as face powder and lipstick (Sharafi *et al.,* 2017; Kim *et al.,* 2015; Karri *et al.,* 2016).

Lead has been referred to as the most toxic chemical contaminant in human history. It has been linked to intrauterine fetal death, premature delivery, and low birth weight due to its ability to cross the placenta during pregnancy. (Anhwange *et al.,* 2013).Cadmium damages blood vessels, heart tissue, kidneys, lungs, and brains, causing heart disease, hypertension, liver damage, and immune system suppression. Cadmium also degrades bones by interfering with calcium metabolism. (Arora *et al.,* 2008). Nickel (Ni) is a ubiquitous metal frequently responsible for allergic skin reactions and has been reported to be one of the most common causes of allergic contact dermatitis (ACD) (Ahmad, 2017).Exposure to high levels of chromium has been linked not only to kidney damage but also to lung and other cancers. Chromium is also linked to skin conditions such as eczema and other inflammations of the skin (Galanis, 2009).

Many researchers have investigated the concentration of heavy metals in cosmetic products commonly used in Nigeria. Nnorom *et al.,* (2011) conducted a study on the concentration of heavy metals in cosmetics used in Nigeria and found that the mean concentration of Pb in three cosmetics products analyzed ranged from 78 to 123 µg/g. Fe (123.08-632.828 µg/g) has the highest mean concentration in the cosmetic products analyzed by Idris *et al.,* (2019). In the cosmetic products investigated by Iweghue *et al.,* (2015), the concentrations of Pb, Cd, Ni and Co were below the specified limit, or the maximal limit for impurities in colour additives in cosmetics for external use. However, Cr was found at concentrations above the allergenic limit

of 1 lg/g. The findings also revealed that skin-lightening creams had higher concentrations of the studied metals than moisturizing creams, with the exception of Ni, implying that people who use skin-lightening creams instead of moisturizing creams are subjected to higher metal concentrations.

Sani *et al.,* (2016) reported the determination of some heavy metals in selected cosmetic products sold in Kano metropolis Nigeria using AAS. The concentration of the heavy metals analyzed are $Mn > Ni > Cu > Cd > Pb > Cr$. The T-test showed no significant difference statistically between higher and lower price cosmetic in terms of the concentration of the heavy metals analyzed.

The aim of this research was to ascertain the concentration level of some heavy metals in commonly used cosmetics (face powders and lipsticks)with a view to providing information on the health risk associated with the application of these cosmetic products.

II. EXPERIMENTAL

Materials and Method

Sample Collection

Cosmetics samples of popular brands of lipstick and powders were collected from three different market locations; Katsina Central Market, Chake Market and Kofar Keke market, each representing key geographical location in Katsina metropolis. Nine samples, three of each mentioned products were purchased from open stores in these markets all within shelf life. In Katsina central market, one of the three samples was purchased at northern gate of the market, another one from the eastern gate and the other sample from western gate near police station. In Chake market, one of the three samples was purchased in the middle of the market, the other along Kofar Guga and the last sample along correction center. In Kofar Keke market one of the three samples was purchased in the middle of the market, another one was purchased near the stadium and the last sample purchased beside general hospital Katsina. Each samples labeled and physical appearance such as colour, manufacturing details, name of products, brand, batch number and ingredients listed on the labels of the products were noted. No two products possessed the same batch number. The samples were coded for easy identification.

Reagents and Chemicals

All the reagents and chemicals used in the study were of analytical grade. HNO_3 (69%, BDH), HCl (36%, Sigma-Aldrich), H_2O_2 (30%, Sigma-Aldrich) and deionized water was used for digestion and dilution of samples and preparation of intermediate metal standard solutions prior to analysis.

Sample Preparation

Sample preparation for the determination of lead, cadmium, nickel and chromium has been carried out according to the method adopted by Balarastaghi *et al.,* (2017). 1g of sample was measured into a conical flask and 15ml of conc. HNO_3 was added followed by 5ml 30% H_2O_2 and then 5ml conc. HCl. The flask was closed for 15min. to ensure complete reaction thus beginning the first phase of acid wet digestion. The resulting mixtures were then heated at 150^0c in a fume hood until no more brown fumes were observed and consequently allowed to cool. After cooling 20ml of deionised water was added and the resulting mixture was filtered through a whatman No.1 filter paper into a 100ml volumetric flask and diluted to volume using de-ionised water before aspiration into the instrument. Digestions were performed in triplicate to ensure accuracy and precision.

Chemical analysis

All digested samples were analyzed in triplicate for Cd, Pb, Ni, and Cr by atomic absorption spectrophotometry. The advisable conditions of analysis and instrument working are mentioned in Tables 2.

Health Risk Assessment of Cosmetic Products

Systemic Exposure Dosage (SED)

The systemic exposure dosage (SED) can be calculated by using the formula:

$$\mathbf{SED} = \frac{\mathbf{CS} \times \mathbf{AA} \times \mathbf{SSA} \times \mathbf{F} \times \mathbf{RF} \times \mathbf{BF}}{\mathbf{BW}} \times \mathbf{10^{-3}}$$

Where Cs and SSA are the heavy metals concentration in the cosmetic product (µg/kg) and the skin surface area (cm^2) onto which the products are applied, respectively. The SSA for face powder and lipsticks is 563 and 4.8 respectively. The AA is the amount of cosmetic used daily. The AA for face powder and lipsticks is 0.51 and 0.057 respectively. RF and F are the retention factor and the frequency of daily use of cosmetics, respectively. The RF value is considered 1. The F for face powder and lipsticks is 2 and 2respectively. BF and BW are the bio accessibility factor and body weight (kg), respectively. The BW value used in this research was 60 kg (El-Aziz *et al*., 2017; Ghaderpoori *et al.,* 2019).

Lowest No Observed Adverse Effect Level (NOAEL)

The NOAEL values were calculated from the oral reference doses (RFDs) using the relationship:

$$\mathbf{NOAEL} = \mathbf{RfD} \times \mathbf{UF} \times \mathbf{MF}$$

The RfD, UF, and MF are the oral reference doses, the uncertainty factor, and the modifying factor, respectively. Based on United States Environmental Protection Agency (USEPA), the RfDs for Cd, Cr, Ni and Pb are 0.001, 0.001, 0.02 and 0.04 respectively. The amount of UF and MF as the default values is 100 and 1, respectively (Ghaderpoori *et al.,* 2019; Idris *et al.,* 2019).

Margin of Safety

The Margin of Safety (MoS) index, an uncertainty factor, was used to assess the risk of contact with heavy metals in cosmetic products as reported by El-Aziz *et al.,* 2017.MoS index is the ratio of NOAEL to

SED day ($\frac{NOAEL}{SED}$). The lowest amount of the MoS is 100 according to WHO and the cosmetic products is safe if MoS value is ≥100.

Hazard Quotients

Hazardous Quotient (HQ) associated with the use cosmetics was determined by the ratio of Systemic Daily Exposure Dose (SED) to the oral reference dose (RfD) for each metal:

$$\frac{\mathbf{SED}}{\mathbf{RfD}}$$

It used to calculate the level of risk. If the HQ value is 1 or less, there is no risk of harm from exposure, and if the HQ value is greater than 1, it is deemed unsafe for human health (Miri et al., 2018; Ghaderpoori *et al.,* 2019).

Hazardous Index (HI)

HI is the sum of the HQ values calculated for all heavy metals:

$$\sum \mathbf{HQ} = \mathbf{HQ_{Pb}} + \mathbf{HQ_{Cd}} + \mathbf{HQ_{Cr}} + \mathbf{HQ_{Ni}}$$

If the HI value < 1, the exposed local population (consumers) is said to be safe; if the HI value ≥ 1, it is considered as not safe for human health (Ghaderpoori *et al.,* 2019)

Carcinogenic risk

Carcinogenic risk is defined as the incremental probability that an individual will develop cancer during one's lifetime due to chemical exposure under specific scenarios (Alam et al., 2019). The CR is obtained by multiplying the SED and the SF ($CR = SED \times SF$). The risk created by a lifetime average amount of 1 mg/kg/day of carcinogenic heavy metals is known as the slope factor. For a carcinogenic element, the allowable or tolerable limits are 0.0001 to 0.000001 (or 10^4–10^6). Copat *et al.,* (2018). The slope factor for Pb is 0.0085, for Cr is 0.5, for Ni is 0.91 and for Cd is 6.7.

III. RESULTS AND DISCUSSION

Table1: Information on the type and Brands of Cosmetics Used for the Study

Face Powder			Lipstick		
Brand Name	Colour	Country	Brand Name	Colour	Country
Iman	Medium	U.S.A	Sleek	Blue	China
Classic	Light	U.S.A	Classic	Red	U.S.A
Milanni	Dark	U.S.A/Italy	Macc	Light nude	Toronto, Canada
Oyly	Dark	China	Black up	Wine	U.S.A
Tara	Medium	P.R.C	Casvyne	Pink	P.R.C
Black up	Dark	U.S.A	Ibeauty	Purple	Paris
Chrising	Dark	U.S.A	Dudu	Maroon	Africa,Nigeria
Casvyne	Medium	P.R.C	Matte	Dark nude	U.A.E
Flameless	Dark	P.R.C	Chanleeve	Orange	China

Table2: Working Conditions for Determination of Concentration of Some Heavy Metals Using Atomic Absorption Spectrophotometer

Metals	Wavelength (nm)	Nebulizer Flow (L/Min)	Type	Read time (s)
Pb	405.781	0.75	Analyte	3
Cr	425.433	0.9	Analyte	3
Cd	228.802	0.5	Analyte	3
Ni	352.454	0.7	Analyte	3

Table 3: Mean Concentration of Heavy Metals in Face powders and Lipsticks

Product Type	Mean Concentration ± Standard Deviation ($mgkg^{-1}$)			
	Pb	Cd	Ni	Cr
Face Powders	0.624±1.508 **(0.101)**	0.007±0.003 **(0.006)**	0.042±0.008 **(0.000)**	0.205±0.089 **(0.178)**
Lipsticks	0.036±0.036 **(0.035)**	0.012±0.009 **(0.007)**	0.033±0.005 **(0.000)**	0.159±0.069 **(0.142)**
WHO	10	0.3	0.6	NA

KEY:

1. NA: Not available
2. The bolded values represent median concentrations.

Table 4: Systemic Exposure Dosage (SED) in ($mgkg^{-1}day^{-1}$)

Product Type	Systemic Exposure Dosage (SED) in ($mgkg^{-1}day^{-1}$)			
	Pb	Cd	Ni	Cr
Face powders	5.47×10^{-3}	6.85×10^{-4}	3.69×10^{-4}	1.79×10^{-4}
Lipsticks	2.99×10^{-8}	9.98×10^{-9}	2.74×10^{-8}	1.32×10^{-7}

Table 5: Calculated Margin of Safety (MoS) for Face Powders and Lipsticks

Product Type	Margin of Safety (MoS)			
	Pb	Cd	Ni	Cr
Face powders	730.37	146.08	5425.67	55.58
Lipsticks	1.34×10^{8}	1.00×10^{7}	7.28×10^{7}	7.56×10^{5}

Table 6: Table of Hazardous Quotient, HQ, and Hazardous Index, HI for the measured Heavy Metals

Product Type	HQ				HI
	Pb	Cd	Ni	Cr	
Face powders	1.37×10^{-1}	6.84×10^{-1}	3.60×10^{-3}	1.79	2.63
Lipsticks	7.48×10^{-7}	9.98×10^{-6}	1.37×10^{-6}	1.32×10^{-4}	1.44×10^{-4}

Table 7: Carcinogenic Risk for Measured Heavy Metals in Face Powders and Lipsticks

Product Type Carcinogenic risk (CR) in ($mgkg^{-1}day^{-1}$)				
	Pb	Cd	Ni	Cr
Face powders	4.64×10^{-5}	4.58×10^{-3}	3.69×10^{-4}	8.95×10^{-5}
Lipsticks	2.58×10^{-8}	6.68×10^{-8}	2.52×10^{-8}	6.60×10^{-8}

Discussion

Eighteen samples of selected cosmetics products, nine each for lipsticks and face powders were analyzed in this study. The mean concentration and median values of the various brands of cosmetics samples were presented in Table 3. The metals studied were Pb, Cd, Ni and Cr. The mean ± SD values for Pb was 0.624±1.508 $mgkg^{-1}$ in face powders and 0.036±0.036 $mgkg^{-1}$ in lipsticks. This values are lower than those reported by (Idris *et al.,* 2019; Hepp, 2012). The content of lead in cosmetic products is also lower than concentration limits set by WHO. In face powder, the mean ± SD of Cd was 0.078±0.003 $mgkg^{-1}$ where in lipsticks was 0.012±0.009 $mgkg^{-1}$. In this study, two samples of these cosmetic products had Cd concentrations below the WHO limit and also below the mean concentration reported by (Balarastaghi *et al.,* 2017) for powder and (Ullah *et al.,* 2018; Sharafi *et al.,* 2017) for lipsticks. The results are close to those reported by (Mohammadi *et al.,* 2013). Nickel mean ± SD values in face powders and lipsticks were 0.042±0.008 $mgkg^{-1}$ and 0.033±0.005 $mgkg^{-1}$. In this study, the face powders have higher concentrations of Ni than the lipsticks. Order of Cr mean concentration ± SD in the samples was powder>lipsticks (0.205±0.089>0.159±0.069). These values are lower than those reported by (Idris *et al.,* 2019). The concentration of the heavy metals analyzed are in the order Pb > Cr > Ni > Cd. Pb has the highest concentration while Cd has the least in both face powders and lipsticks.

The SED values for Pb, Cd,Ni and Cr in face powders and lipsticks were $5.47\times10^{-3}mgkg^{-1}day^{-1}$ and $2.99\times10^{-8}mgkg^{-1}day^{-1}$, $6.85\times10^{-4}mgkg^{-1}day^{-1}$ and $9.98\times10^{-3}mgkg^{-1}day^{-1}$, $3.69\times10^{-4}mgkg^{-1}day^{-1}$ and $2.71\times10^{-8}mgkg^{-1}day^{-1}$, 1.79×10^{-4} $mgkg^{-1}day^{-1}$ and $1.32\times10^{-7}mgkg^{-1}day^{-1}$ respectively. When compared with the provisional tolerable daily intake (PTDI), which were 3.6 $\mu gkg^{-1}bwday^{-1}$ for Pb, 1 $\mu gkg^{-1}bwday^{-1}$ for Cd, 720 $\mu gkg^{-1}bwday^{-1}$ and 200 $\mu gkg^{-1}bwday^{-1}$, the SED values are very much lower. This result is in agreements with the values obtained by (Arshad *et al.,* 2020; Ababneh and Al-Momani, 2018).

From Table 5, the MoS value calculated for Pb, Cd, Ni and Cr in powder and lipsticks were 730.34 and 1.34×10^{8}, 146.08 and 1.00×10^{8}, 5425.67 and 7.28×10^{8}, 55.58 and 7.56×10^{8} respectively. According to WHO proposal in order to safely use cosmetics, the MoS index should be≥100 (El -Aziz et al., 2017). From the results, the values obtained are higher than the standard values except for Cr in face powders and also higher than the values obtained by (Idris *et al.,* 2019).

Table 6, shows the Hazard Quotient (HQ) and Hazard indices (HI) of oral and dermal pathways in the sample of face powders and lipsticks studied. This study reveals that the HQ values forPb, Cd, NI, and Cr in face powders and lipsticks are 1.37×10^{-1} and 7.48×10^{-7}, 6.84×10^{-1} and 9.98×10^{-6}, 3.6×10^{-3} and $1.37\times10^{-7,}$ 1.79×10^{0} and 1.32×10^{-4} respectively. It is apparent that the HQ of all the metals except Cr in face powder indicating that there is low risk of detrimental effect. The amount of HI in face powder is greater than one(Table

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6), indicating that prolonged use of face powder is not safe, and this result is close to the result presented by El-Aziz *et al*., (2017). But for lipstick the value is less than one which is safe for use and this result is concordant with that of (Alam *et al*., 2019: Arshad *et al.,* 2020).

Pb, Cd, Ni, and Cr are listed as carcinogenic heavy metalsby International Agency for Research on Cancer (IARC, 2012). Heavy metals can reach the body via 2 significant routes: ingestion or dermal absorption. Heavy metals are non-biodegradable so they remain accumulated into the body for long period. As a result, they do not only alter the cell functions but also cause disruption of intercellular mechanisms. Therefore cancer related diseases are enhanced by such impurities that cause oxidative stress, DNA damage and cell death (Kim *et al*., 2015). Cancer Risk (CR) is a calculation of the user's possible cancer risk as a result of exposure to heavy metals in cosmetic products. The appropriate range for CR, according to the USEPA, is 1×10^{-6} to 1×10^{-4} (Arshad *et al*., 2020). Among all the analyzed heavy metals (Table 7) cancer risk was estimated lower than the permissible limit except cadmium (Cd) in face powder, which is higher than the permissible limit and the cosmetic products may not possess cancer risk except cadmium in face powder. The result are in concordant with that of (Lim *et al.,* 2018: Zakari *et al.,* 2015) in lipsticks and that of (El-Aziz *et al.,* 2017: Mansouri *et al.,* 2018) in face powders.

IV. CONCLUSION

This study revealed that the concentration of Pb, Cd, Ni, and Cr in both face powders and lipsticks were below permissible limit set by WHO. According to WHO proposal in order to safely use cosmetics the MoS index should be≥100. From the results obtained the values were higher than the standard value except for chromium in face powder. The SED values for all the heavy metals were much lower than the provisional tolerable daily intake (PTDI). The HQ of all the metal except chromium in face powders were within the permissible limit while the HI value in face powder were above permissible limit and below in lipsticks. The carcinogenic risk (CR) values estimated were lower than the permissible limit except cadmium in face powder. Despite the fact that concentration of metals reported were lower than the permissible limit, daily exposure can cause cumulative effect which lead to cancer and other health disorders. This study recommends continuous monitoring of heavy metals and chemicals used in the manufacture of cosmetic products and public enlightment on the harmful effect of excessive use of cosmetics.

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CONFLICTS OF INTEREST

The authors declare no conflict of interest of any form.

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