Risk Assessment of Selected Heavy Metals in Facial Make-up Cosmetics Commonly Used in Ibadan, Oyo State, Nigeria

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Abstract

Facial make-up cosmetics have been reported to consist of some toxic metals. This study was carried out to determine the level of heavy metals in different facial make-up cosmetics such as powder, foundations, mascara, lipsticks and eyeshadow purchased from a local market in Ibadan, Oyo State, Nigeria to estimate the potential risk associated with them. Samples were acid digested on a hotplate using a combination of acids ($HNO_3/H_2SO_4/HClO_4$) in the ratio 1:1:1. Cd, Cr, Cu, Ni, Zn and Pb were analyzed using Buck Scientific Model 230 atomic absorption spectrometry (AAS). Generally, it was observed from the results that cadmium and nickel were below detectable limit in 100% of the cosmetics whereas copper, chromium and zinc were detected in most samples in the following range: 0.589-17.627 mg/kg, 0.157-0.270 mg/kg, 0.870-3.478 mg/kg, in foundation, 0.225-0.515 mg/kg, 0.147-0.254 mg/kg, 0.718-2.274 mg/kg, in powder; 0.688-16.503 mg/kg, 0.115-0.340 mg/kg ,0.816-9.932 mg/kg, in eyeshadow. However, lead (Pb) was found at very low concentrations in some samples of powder, lipstick and mascara as follows; 0.176 -0.216 mg/kg; 0.369-0.656 mg/kg and 0.367-0.680 mg/kg respectively when compared with permissible limits. The human health risk was estimated by employing the systemic exposure dosage and Margin of Safety as risk indicators. Cu and Pb in most cosmetic samples and Cr in powder confirmed MoS values below 100% bioaccessibility, an indication that they are not safe for use. The findings revealed that some of the cosmetics contain low concentrations of heavy metals which accumulate in biological systems over time with continuous usage of the products, hence, regulatory agencies in the country are urged to take proper action to monitor and regulate the levels of toxic metals in imported cosmetic products to ensure consumers' safety and safeguard public health.

Keywords: Heavy metals, Cosmetics, Health risk, Margin of Safety, Atomic absorption spectrophotometer

1. Introduction

Cosmetics are considered to be any materials administered on the various external parts of the body such as skin, face, hair, lips and nails mostly for the purpose of cleaning, beautification, perfuming, protection, changing their appearance, correcting body odour and keeping the surfaces in good condition [2,22] Nowadays, the use of cosmetic products for personal grooming and body beautification has become the norm especially for women world-wide [23]. The market of facial makeup cosmetics is thriving at a very rapid rate globally over the past few decades with mean growth of 5% annually [7,18]. The raw materials and production processes for cosmetics have also evolved, from small-scale using only natural ingredients, to mass production and the inclusion of synthetic materials such as petrochemicals, pigment and preservatives which contain some traces of heavy metals particularly copper, chromium, lead, zinc, nickel, mercury and cobalt [9]. Heavy metal in cosmetics is of great concern due to the biodegradation nature, biological accumulation and toxicity in human body [15]. Although the use of metals as ingredients in cosmetics is prohibited in many advanced countries, metallic impurities cannot be avoided, even under good manufacturing practice, because they exist naturally in the environment [4]. It was discovered that metals may accumulate on the skin with regular use of contaminated cosmetics, resulting to long-term exposure of the individual to the metal, even when such cosmetics are no longer applied [12]. The majority of human problems associated with of lead poisoning are stomach pain, unconsciousness, anaemia, fertility problems; nervous system disorders [20]. Cadmium is also present in many cosmetics products but most especially in lipsticks and face powders. It is used mainly as a colour pigment in

many cosmetics industries. The diseases that result due to exposure to cadmium include cardiovascular diseases, diabetes and hypertension [3]. In most countries, it is legally prohibited to use lead, arsenic, cadmium and mercury in skin cosmetic products [15]. Dermal exposure is expected to be the most prominent route for cosmetic products since almost all cosmetics are applied on the skin. Oral exposure can occur for cosmetics (e.g. lipstick or lip gloss) used in and around the mouth as well as from hand to mouth contact after exposure to cosmetics containing heavy metal impurities. However, inhalation exposure is normally considered to be negligible [1,5].

As specified by Health Canada, cosmetics products contain at least 4 of the 8 metals of concern (arsenic, cadmium, lead, mercury, beryllium, nickel, selenium, and thallium) [13]. Heavy metals content in most cosmetic products manufactured and sold in many developed nations are prohibited or at least restricted, even though regulations are varied and threshold levels allowed by particular regulations are different for various products and countries.

A study by [21] on the levels of lead, cadmium, nickel, chromium, and mercury was conducted have been assessed in 28 body creams and lotions, 10 powders, 3 soaps, 5 eye make-ups, and 4 lipsticks widely available on Nigerian markets. The increases over suggested or mandated levels of lead in these creams and lotions ranged from 6.1 to 45.9 and from 1.2 to 9.2 mg kg^{-1} when compared with Cosmetic Ingredients Review Expert Panel 2007 and German safe maximum permissible limit of lead in cosmetics, respectively. Chromium and mercury were undetected in 100% of the cosmetic product. A similar study [8] also revealed that in a total of 40 samples consisting of 10 different types of facial cosmetics commonly used in Nigeria, Chromium, nickel, zinc and iron were found in varying concentrations in all the samples, 85% of the samples also contain Cd while 18 of the 40 samples have Pb above detection limit (0.20–31.70 mg kg^{-1}).

The Cosmetic Ingredient Review Expert Panel established by Food and Drug Administration (FDA) in the USA has set a permissible limit for some metals; As (5 mg/kg), Pb (10 mg/kg), other heavy metals (20 mg/kg) [29]. The European Union's limits for Pb, Cd and chromium are 0.5, 0.5 and 1.0 mg/kg, respectively. The World Health Organisation (WHO) also set maximum levels for Pb (10 mg/kg), Cd (0.3 mg/kg) and Hg (1 mg/kg). [11,14]. Most facial make-up cosmetics are being sold under the brand name of well reputed national and international companies in both open markets and superstores in the country [28]. The need arises to investigate the levels of the heavy metals in the cosmetics in Ibadan metropolis due to high patronage of the products by people for beautification purposes. This research therefore aims to determine the concentration of heavy metals in cosmetics purchased from beauty shops at Orita local market in Ibadan, Oyo state, Nigeria using the margin of safety as risk indicators to assess the potential exposure risks to prospective consumers.

2. Materials and Methods

2.1 Sample Collection

Twenty cosmetic products in the form of eyeshadows, lipsticks, powder, mascara and foundation were purchased from beauty stores at Orita local market in Ibadan, Oyo state Nigeria. The descriptions of the cosmetic samples are displayed in Table 1.

Table 1: Description of Cosmetic Products Purchased from Orita Market in Ibadan

Sample Name	Sample Code	Colour	Country of Manufacture
Eyeshadow	EU	8 Colours	China
	ERS	Green	China (P.R.C)
	EM	8 Colours	United Kingdom
	EMB	10 Colours	United Kingdom
Powder	PM	Brown	Italy
	PI	Brown	China
	PKB	Brown	China
	PEB	Brown	China (P.R.C)
Lipstick	LMB	Brown	USA
	LM	Red	China
	LU	Wine	China
	LC	Wine	USA
Foundation	FBA	Brown	China
	FA	Brown	China
	FBC	Brown	China
	FS	Brown	China
Mascara	MV	Black	China
	MMP	Black	Paris
	MM	Black	China
	MMB	Black	China

2.2 Reagents and Chemicals

All glassware used for this research were pre-washed with liquid detergent and rinsed twice with water. Afterwards, they were placed in a solution of 5% HNO_3 overnight, rinsed with distilled water and dried ready for use. Nitric acid (HNO_3), Sulphuric acid (H_2SO_4) and Perchloric acid ($HClO_4$) used were of analytical-reagent grade manufactured by Merck, Germany. Each sample digestion was performed in duplicate and blank samples were also prepared. Distilled water was utilized for all solution dilution and preparation of calibration standards used during AAS analysis of extracts.

2.3 Sample Preparation and Analysis

The cosmetic samples were crushed to powdered form using mortar and pestle and dried in the oven at 105^0C for 2 hr. Each sample was digested in duplicate by weighing 1.0 g of sample into 100 mL conical flask using a mixture of acid (HNO_3, H_2SO_4 and $HClO_4$ in ratio of 1:1:1) following the procedure by [7,26] with a little modification. 5 mL of HNO_3 was added to each sample and the mixture kept overnight in the fume cupboard at room temperature. Subsequently, the contents were heated on a hot plate to about dryness for 1 hour by slowly increasing the temperature to 90℃ and mixture allowed to cool. H_2SO_4 (5 mL) was then added and the solution heated again for 30 min followed by cooling to room temperature. Finally, 5 mL of $HClO_4$ was added and the mixture digested until clear solution was obtained. After digestion, the samples were cooled, few drops of distilled water added and the solution filtered through Whatman filter paper No. 41 to final volume of 50 mL in a volumetric flask with distilled water. The digested sample extracts were taken for metal analysis using Bulk Scientific Model 230 Atomic Absorption Spectrophotometer. Measurements were made under optimized operating conditions of the flame atomic absorption spectrophotometer (FAAS). The working standard solutions for the calibration of the FAAS were prepared daily from stock solutions (1,000 mg/ L) with distilled water used for dilutions. The wavelength for the determination of cadmium was 227 nm, copper

324.8 nm, chromium 356 nm, lead 283 nm, nickel 286 nm, and zinc 213.9 nm respectively.

Determination of pH

10 g of cosmetic sample was weighed into a 100mL beaker and 10 mL deionized water was added into it. The sample mixture was stirred for 1 hour on a mechanical shaker, allowed to stand for 30 min and the pH value measured by inserting the electrode of the pH meter which has been calibrated with buffer 4, 7 and 9.

2.4 Health Risk Assessment

Margin of Safety (MoS)

The potential human health risk associated with exposure to heavy metals in cosmetics can be evaluated in terms of Margin of Safety (MoS), calculated by taking a ratio of No Observed Adverse Effect Level (NOAEL) of the product under study by its systemic exposure dosage (SED) as reported by [26]. [6,17]

$$\text{MoS} = \frac{NOAEL}{SED}$$

The SED forecasts the level of metals that are taken into the body by several exposure routes. The calculation is dependent on the amount of metal present in the cosmetic, quantity of the cosmetic applied per day, frequency of application, surface area of the skin on which the product is applied and average body weight [6,17]

The SED value was calculated as follows;

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

where, Cs denotes metal concentration in the sample in mg/kg, SSA is the surface area of skin onto which the sample is applied (cm^2), AA shows the amount applied (g/cm^2), RF is the retention factor, F denotes the application frequency of a product /day, BF is the bio-accessibility factor, 10^{-3} in mg/kg is used as unit conversion factor and BW is the average body weight (60 kg) [10, 26]

A level of exposure where no adverse effect is seen is called NOAEL and its value was calculated based on dermal reference doses (RfD) as reported by using the equation:

NOAEL= RfD x UF x MF

where, UF is uncertainty factor (reflects overall confidence in the various data sets), MF is modifying factor. Default values for MF and UF are 1 and 100 respectively. RfD denotes dermal reference doses (mg kg^{-1} d^{-1}) of different metals. According to World Health Organization (WHO), MoS value up to 100 is acceptable and product with MoS value above 100 is considered safe for use. The scientific committee on consumer's safety (SCCS) recognizes that in many conventional calculations of MoS, oral bioavailability of an element is assumed to be 100%, if oral absorption data are not available. Standard values of skin surface area (SSA) and amount applied (AA) established by SCCS for cosmetic products. However, it is considered suitable to assume that not more than 50% of an orally administered is systematically accessible [6,17,26]

3. Results and Discussion

Determination of pH

The values obtained for pH measurement are as represented in Figure 1. It was observed that cosmetic samples such as foundation and lipstick had pH values in the range 5.60 – 5.93, which implies their acidic nature, while eyeshadow, mascara and powder had pH values in the range 6.71 – 10.8, which implies that they fall within neutral to alkaline. The skin's natural pH is slightly acidic **(pH 5.5),** but they could be as low as 4.5 and as high as 7. Most of the cosmetic samples fall within this range with the exception of mascara and eyeshadow in few cases.

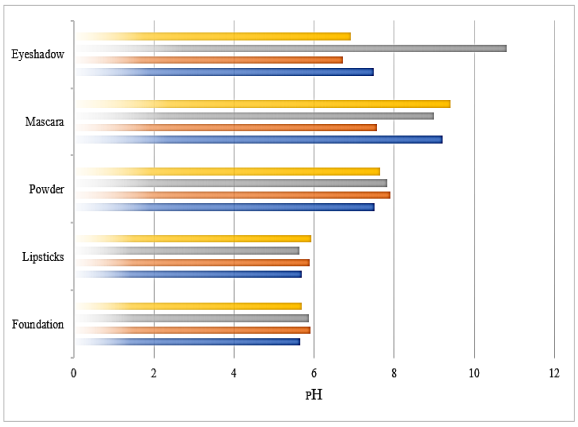

Figure 1: pH of Cosmetic products.

Table 2: Heavy Metal Concentration in Cosmetic Products

Cosmetics	Sample Code	Cu	Zn	Cr	Cd	Pb	Ni
Foundation (mg/kg)	FS	17.627	2.675	0.221	BDL	BDL	BDL
	FA	2.836	0.902	0.270	BDL	BDL	BDL
	FBA	0.598	3.478	0.057	BDL	BDL	BDL
	FBC	1.484	0.870	0.177	BDL	BDL	BDL
	Mean	5.636	1.981	0.181	BDL	BDL	BDL
	Std Dev.	8.046	1.306	0.091	BDL	BDL	BDL
Lipstick (mg/kg)	LMB	0.431	0.754	BDL	BDL	0.656	BDL
	LC	0.911	0.613	BDL	BDL	0.369	BDL
	LM	0.513	0.637	BDL	BDL	0.000	BDL
	LU	0.259	0.117	BDL	BDL	0.407	BDL
	Mean	0.528	0.530	BDL	BDL	0.358	BDL
	Std. Dev.	0.276	0.282	BDL	BDL	0.271	BDL
Powder (mg/kg)	PM	0.515	2.274	0.254	BDL	BDL	BDL
	PI	0.225	1.450	0.242	BDL	0.210	BDL
	PKB	0.424	0.718	0.147	BDL	0.176	BDL
	PEB	0.276	1.039	0.000	BDL	0.000	BDL
	Mean	0.360	1.370	0.161	BDL	0.097	BDL
	Std..Dev	0.134	0.673	0.118	BDL	0.112	BDL
Mascara (mg/kg)	MMP	0.483	0.620	BDL	BDL	0.680	BDL
	MV	0.462	0.509	BDL	BDL	0.608	BDL
	MMB	0.356	0.454	BDL	BDL	0.367	BDL
	MM	0.295	3.684	BDL	BDL	0.463	BDL
	Mean	0.399	1.317	BDL	BDL	0.529	BDL
	Std Dev.	0.089	1.579	BDL	BDL	0.141	BDL
Eyeshadow (mg/kg)	ERS	16.503	6.705	BDL	BDL	BDL	BDL
	EM	0.978	1.083	BDL	BDL	BDL	BDL
	EU	0.688	0.816	0.340	BDL	BDL	BDL
	EMB	1.023	9.932	0.115	BDL	BDL	BDL
	Mean	4.798	4.634	0.110	BDL	BDL	BDL
	Std. Dev.	7.800	4.460	0.160	BDL	BDL	BDL
Permissible Limits	**WHO (Health Canada)**	**-**	**-**	**-**	**0.3**	**10**	**0.6**
	EU	**-**	**-**	**1.0**	**0.5**	**0.5**	**-**

*BDL denotes Below Detectable Limit

4. Discussion

The results of levels of heavy metals in four brands of foundation are summarized in Table 2. Varying levels of Cu was found among the samples of foundation, with FS having the highest Cu level (17.627 mg/kg) and FBA the lowest (0.598 mg/kg). Zinc level was found to be highest in FBA (3.478 mg/kg), The range of values obtained were in the order; FBC> FA > FS> FBA. Similarly, there was no significant difference in Cr concentration obtained for foundation samples sample (0.221, 0.270, 0.057 and 0.177 mg/kg), the range of values were in descending order FBA>FBC>FS. Whereas, level of Cr in FBA was the lowest (0.057 mg/kg), FA (0.270 mg/kg) had the highest Cr. However, metals Cd, Pb and Ni were not detected in any of the samples of foundation analysed. In four different brand of lipstick, copper level was found to be higher in LC (0.911 mg/kg), while LU (0.259mg/kg) was lowest concentration. Zn concentration ranged from 0.117 - 0.754 mg/kg, LMB had highest Pb, it was not found in LM. Cr, Cd and Ni was not present in any of the lipstick samples. The results of this study were similar (especially for Cu and Cr) when compared with the report obtained by [28] which revealed concentration ranges in lipsticks in the range 2.45–22.06, 0–11.03, 4.24–12.71, 0.07–1.67, 0–0.05 and 0–0.19 mg kg^{-1} for Mn, Ni, Cu, Cd, Cr and Pb respectively.

The results of levels of heavy metals in four brands of powder are displayed in Table 2. Among the different brands of powder, PM had highest concentration of Cu (0.515 mg/kg), followed by PKB (0.424 mg/kg), PEB (0.276 mg/kg) and PI (0.225 mg/kg). Highest concentration of Zn (2.274 mg/kg), Cr (0.254 mg/kg) were detected in PM, but not in PM and PEB. Pb was detected in PI (0.21mg/kg) and PKB (0.176mg/kg), Cd and Ni were not detected in any of the powder samples. This results were similar to the range of values obtained by [28] in face powders; 4.90–44.12, 3.68–11.03, 4.24–8.48, 0.07–1.74, 0–0.03 and 0.08–0.33 mg kg^{-1} for Mn, Ni, Cu, Cd, Cr and Pb respectively. The results of heavy metals in four brands of mascara showed that Cu in mascara samples to be in the range 0.483 to 0.295 mg/kg. Highest Zn was detected in MM (3.684 mg/kg) and the highest Pb was detected in MMP (0.680 mg/kg), while the lowest Zn and Pb was detected in MMB (0.454 and 0.367 mg/kg). While Cr, Cd and Ni was not detected in any of the mascara samples.

The results of levels of heavy metals in four brands of eyeshadow showed wide variation of Cu concentrations (16.503,0.978,0.688 and 1.023 mg/kg) was observed among the samples of eyeshadows. Where ERS has the highest Cu (16.503 mg/kg). The highest Zn was found in EMB (9.932 mg/kg). In the rest of samples Zn was found in the order: EU > EM > ERS. Only EU and EMB were detected for Cr, with values 0.340 and 0.115 mg/kg respectively. Cd, Pb and Ni was not detected in any of the eyeshadow samples.

5. Statistical Analysis

6. To determine the relationships between the heavy metals, Pearson correlation statistics (Table 3) was used. Correlation between heavy metals in foundation showed a strong negative correlation between Zn and Cr. In powder, strong positive correlation existed between Zn/Cr and Cr/Pb. In Mascara, strong negative correlation existed between Cu and Zn while there was strong positive correlation between Cu and Pb. The correlation coefficient value between Cu and Zn was 0.32 in Eyeshadow.

Table 3: Correlation Coefficient Values between the Heavy Metals in Cosmetics

Cosmetics	Sample Code	Cu	Zn	Cr	Cd	Pb	Ni
Foundation (mg/kg)	Cu	1	-	-	-	-	-
	Zn	0.3	1	-	-	-	-
	Cr	0.4	-0.7	1	-	-	-
Lipstick (mg/kg)	Cu	1	-	-	-	-	-
	Zn	0.5	1	-	-	-	-
	Pb	-0.2	0	-	-	1	-
Powder (mg/kg)	Cu	1	-	-	-	-	-
	Zn	0.4	1	-	-	-	-
	Cr	0.3	0.7	1	-	-	-
	Pb	0.1	0.2	0.9	-	1	-
Mascara (mg/kg)	Cu	1	-	-	-	-	-
	Zn	-0.8	1	-	-	-	-
	Pb	0.8	-0.3	-	-	1	-
Eyeshadow (mg/kg)	Cu	1	-	-	-	-	-
	Zn	0.3	1	-	-	-	-

The concentration of Cu and Zn in the analysed cosmetics was graphically presented with Fig. 2 showing a strong positive linear relation with few exceptions.

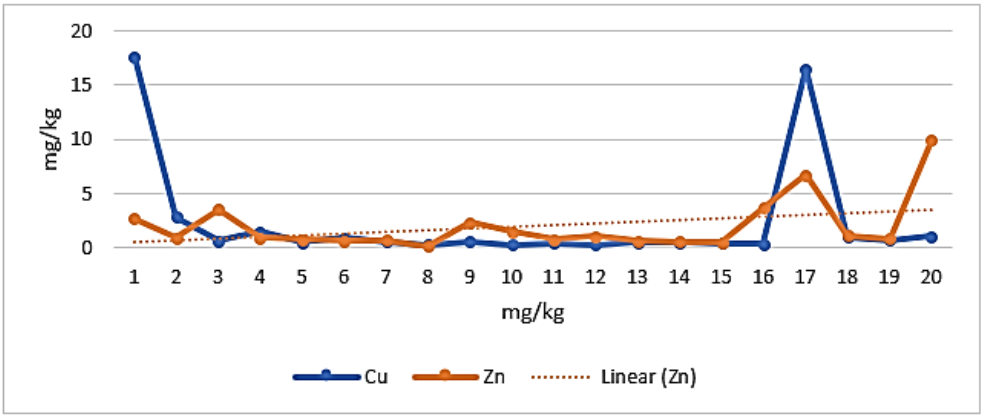

Figure 2: Line chart showing correlation between the concentration of Cu and Zn.

Table 4: Correlation Coefficient Values between pH and Heavy Metals Content in Cosmetics

Cosmetics		pH	Cu	Zn	Cr/Pb	Cosmetics		pH	Cu	Zn	Cr	Pb
Foundation (mg/kg)	**pH**	1				Powder (mg/kg)	**pH**	1				
	Cu	-0.64	1				**Cu**	-0.63	1			
	Zn	-0.03	0.3	1			**Zn**	-0.64	0.4	1		
	Cr	-0.1	0.4	-0.7	1		**Cr**	0.06	0.3	0.7	1	
Lipstick (mg/kg)	**pH**	1					**Pb**	0.99*	0.1	0.2	0.9	1
	Cu	0.07	1			Mascara (mg/kg)	**pH**	1				
	Zn	-0.73	0.5	1			**Cu**	-0.52	1			
	Pb	-0.52	-0.2	0	1		**Zn**	0.5	-0.8	1	-	
Eyeshadow (mg/kg)	**pH**	1			-		**Pb**	-0.31	0.8	-0.3	-	1
	Cu	-0.19	1		-							
	Zn	-0.51	0.3	1	-							

Pearson correlation statistics (Table 4) was used to determine the relationships between the pH values and the heavy metal concentrations from the samples. Generally, there was no significant correlation between the pH values and the heavy metals detected. However, a very strong positive correlation was observed between pH/Pb in Powder and a strong negative correlation was observed between pH/Cu and Zn/Cr in Foundation. In powder, strong positive correlation also existed between Zn/Cr and Cr/Pb. In Mascara, strong negative correlation existed between Cu/Zn, while there was strong positive correlation between Cu/Pb. The correlation coefficient value between pH/Zn was -0.51 in Eyeshadow.

The correlation of Cu between the different cosmetics revealed a very strong correlation between Foundation and Eyeshadow (r = 0.99). Pb was BDL in both cosmetics. Also, strong correlation was observed between Foundation/ Powder (r = 0.7) and Foundation/Mascara (r = 0.68). There was however a very low negative correlation between Cu in Foundation and Lipstick (-0.16). Both cosmetics had a mean pH of 5.8 indicating they are both slightly acidic.

Health Risk Assessment

Table 5: Systemic Exposure Dosage (SED) Values of Heavy Metals in Cosmetics

Mascara	**Cu**	**Zn**	**Cr**	**Pb**	**Cd**	**Ni**
50% bio-accessibility						
MMP	$2.99x10^{-2}$	$3.8x10^{-2}$	-	$4.2x10^{-2}$	-	-
MV	$2.9x10^{-2}$	$3.2x10^{-2}$	-	$3.8x10^{-2}$	-	-
MMB	$2.2x10^{-2}$	$2.8x10^{-2}$	-	$2.3x10^{-2}$	-	-
MM	$1.8x10^{-2}$	$2.28x10^{-1}$	-	$2.9x10^{-2}$	-	-
Powder	**Cu**	**Zn**	**Cr**	**Pb**	**Cd**	**Ni**
50% bio-accessibility						
PM	$3.2x10^{-2}$	$1.4x10^{-1}$	$1.6x10^{-2}$	-	-	-
PI	$1.4x10^{-2}$	$8.9x10^{-2}$	$1.5x10^{-2}$	$1.3x10^{-2}$	-	-
PKB	$2.6x10^{-2}$	$4.4x10^{-2}$	$9.10x10^{-3}$	$1.1x10^{-2}$	-	-
PEB	$1.7x10^{-2}$	$6.4x10^{-2}$	-	-	-	-
Foundation	**Cu**	**Zn**	**Cr**	**Pb**	**Cd**	**Ni**
50% bio-accessibility						
FS	$1.0x10^{-1}$	$1.66x10^{-1}$	$2.96x10^{-5}$	-	-	-
FA	$1.76x10^{-1}$	$5.6x10^{-2}$	$1.7x10^{-2}$	-	-	-
FBA	$3.7x10^{-2}$	$2.15x10^{-1}$	$3.53x10^{-3}$	-	-	-
FBC	$9.2x10^{-2}$	$5.4x10^{-2}$	$1.1x10^{-2}$	-	-	-
Eyeshadow	**Cu**	**Zn**	**Cr**	**Pb**	**Cd**	**Ni**
50% bio-accessibility						
ERS	1.0x10-1	$4.15x10^{-1}$	-	-	-	-
EM	$6.1x10^{-2}$	$6.7x10^{-2}$	-	-	-	-
EU	$4.3x10^{-2}$	$5.1x10^{-2}$	$2.1x10^{-2}$	-	-	-
EMB	$6.33x10^{-1}$	$6.15x10^{-1}$	$7.12x10^{-3}$	-	-	-
Lipstick	**Cu**	**Zn**	**Cr**	**Pb**	**Cd**	**Ni**
50% bio-accessibility						
LMB	$6.27x10^{-1}$	$4.7x10^{-2}$	-	$4.1x10^{-2}$	-	-
LC	$5.6x10^{-2}$	$3.8x10^{-2}$	-	$2.3x10^{-2}$	-	-
LM	$3.18x10^{-3}$	$3.9x10^{-2}$	-	0	-	-
LU	$1.6x10^{-2}$	$1.1x10^{-2}$	-	$2.5x10^{-2}$	-	-

The calculated values obtained for systemic exposure dosage (SED) at 50% for the heavy metals in different cosmetic products are as summarised in Table 5. From the results, it was observed that at 50% bio-accessibility, SED values for Cu, Zn and Pb in samples of Mascara, ranged from 2.99 $x10^{-2}$ - 2.9 $x10^{-2}$ mg/kg, 3.8 $x10^{-2}$ - 2.28 $x10^{-1}$ and 4.2 $x10^{-2}$ - 3.8 $x10^{-2}$ mg/kg/d respectively.

In the samples of powder, the SED values for Cu, Zn, Cr and Pb had values from $3.2x^{-2}$ - $2.6x10^{-2}$ mg/kg, $8.9x10^{-2}$ - 1.4 $x10^{-1}$ mg/kg, $9.10x10^{-3}$ - $1.6x10^{-2}$ mg/kg and $1.3x10^{-2}$ - $1.1x10^{-2}$ mg/kg respectively. In samples of foundation, the calculated SED values for Cu, Zn and Cr ranged from 9.2 $x10^{-2}$ - 1.76 x 10^{-1}mg/kg, 5.6 x 10^{-2} - 2.15 $x10^{-1}$ mg/kg and 2.96 $x10^{-5}$ to 1.7 $x10^{-2}$ mg/kg respectively. Likewise, for eyeshadow samples estimated SED values for Cu, Zn and Cr ranged from $6.1x10^{-2}$ - $6.33x10^{-1}$, $6.7x10^{-2}$ - $6.13x10^{-1}$ mg/kg and $7.12x10^{-3}$ - $2.1x10^{-2}$ mg/kg respectively.

For lipstick samples, the calculated SED values for Cu, Zn and Pb were as follows; $3.18x10^{-3}$ - $6.27x10^{-1}$ mg/kg, $4.7x10^{-2}$ - $3.9x10^{-2}$mg/kg and $4.1x10^{-2}$ - $2.5x10^{-2}$ mg/kg. The values for SED in this study for cosmetic products analyzed were observed to be a little higher when compared to those reported in previous studies by [6,10,16]

Table 6: Margin of Safety (MoS) for Heavy Metals in Cosmetic Samples

Lipstick	**Cu**	**Zn**	**Cr**	**Pb**	**Cd**	**Ni**
50% bio- accessibility						
LMB	$6.3x10^{0}$	-	-	$9.7x10^{0}$	-	-
LC	$7.1x10^{1}$	-	-	$1.7x10^{1}$	-	-
LM	$1.3x10^{-3}$	-	-	-	-	-
LU		-	-	$1.6x10^{1}$	-	-
100% bio-accessibility						
LMB	-	$6.38x10^{2}$	-	-	-	-
LC	-	$7.89x10^{2}$	-	-	-	-
LM	-	$7.69x10^{2}$	-	-	-	-
LU	$2.50x10^{2}$	$2.727x10^{3}$	-	-	-	-
Mascara	**Cu**	**Zn**	**Cr**	**Pb**	**Cd**	**Ni**
50% bio-accessibility						
MMP	$1.3x10^{1}$	-	-	$9.5x10^{0}$	-	-
MV	-	-	-	$1.0x10^{1}$	-	-
MMB	-	-	-	$1.7x10^{1}$	-	-
MM	-	-	-	$1.3x10^{1}$	-	-
100% bio-accessibility						
MMP	-	$7.89x10^{2}$	-	-	-	-
MV	$1.37x10^{2}$	$9.37x10^{2}$	-	-	-	-
MMB	$1.81x10^{2}$	$1.071x10^{3}$	-	-	-	-
MM	$2.22x10^{2}$	$1.31x10^{2}$	-	-	-	-
Powder	**Cu**	**Zn**	**Cr**	**Pb**	**Cd**	**Ni**
50% bio-accessibility						
PM	-	-	$1.8x10^{1}$	-	-	-
PI	-	-	$2.0x10^{1}$	$3.0x10^{1}$	-	-
PKB	-	-	$3.296x10^{-5}$	$3.6x10^{1}$	-	-
PEB	-	-	-	-	-	-
100% bio-accessibility						
PM	$1.25x10^{2}$	$2.21x10^{2}$	-	-	-	-
PI	$2.85x10^{2}$	$3.37x10^{2}$	-	-	-	-
PKB	$1.53x10^{2}$	$6.81x10^{2}$	-	-	-	-
PEB	$2.35x10^{2}$	$4.68x10^{2}$	-	-	-	-
Foundation	**Cu**	**Zn**	**Cr**	**Pb**	**Cd**	**Ni**
50% bio-accessibility						
FS	$3.6x10^{0}$	-	$1.01x10^{-6}$	-	-	-
FA	$2.2x10^{1}$	-	$1.7x10^{1}$	-	-	-
FBA.		-	$8.50x10^{-5}$	-	-	-
FBC	$4.3x10^{1}$	-	$2.7x10^{1}$	-	-	-
100% bio-accessibility						
FS	-	$1.80x10^{2}$	-	-	-	-
FA	-	$5.35x10^{2}$	-	-	-	-
FBA	$1.08x10^{2}$	$1.39x10^{2}$	-	-	-	-
FBC	-	$5.55x10^{2}$	-	-	-	-
Eyeshadow	**Cu**	**Zn**	**Cr**	**Pb**	**Cd**	**Ni**
50% bio-accessibility						
ERS	$3.9x10^{0}$	$7.2x10^{1}$	-	-	-	-
EM	$6.5x10^{1}$	-	-	-	-	-
EU	$9.3x10^{1}$	-	$1.4x10^{1}$	-	-	-
EMB	$6.3x10^{0}$	$4.8x10^{1}$	$4.21x10^{-5}$	-	-	-
100% bio-accessibility						
ERS	-	-	-	-	-	-
EM	-	$4.47x10^{2}$	-	-	-	-
EU	-	$5.88x10^{2}$	-	-	-	-
EMB	-	-	-	-	-	-

The estimated levels of MoS applied to estimate the potential human health risk of heavy metals at 50% and 100% bio-accessibility are as displayed in Table 6. It was observed that MoS values obtained in foundation samples for Cu and Cr were below 100% which indicate that they are not safe to use. However, the MoS values for Zn and FAB in Cu were above 100% which revealed that they safe for use. Similarly, in lipstick, Cu and Pb had values less than 100%, an indication that they are not safe to use, however, the MoS value for Zn and Cu in sample LU was above 100% which implies that they are innocuous and can be used by consumers. For the samples of mascara, Pb and Cu in MMP had MoS values below 100% which indicate that they are safe for use, whereas the MoS value for Zn and Cu was greater than 100% which make it safe for use. In the samples of powder, Cr and Pb had values less than 100% hence, they are not safe to use. The MoS value for Zn and Cu was higher than 100%, making it safe for use. In the samples of eyeshadow, Cu, Zn and Cr had values lower than 100% which indicate that they are not safe for use. The MoS values for Zn (EM and EU) were greater than 100% which make it safe for use.

Conclusion

This study determined the levels of heavy metals such as lead, cadmium, copper, chromium, zinc and nickel in facial cosmetics and results obtained revealed that cadmium and nickel were not detected in any of the cosmetics samples, however, some concentration of lead, copper, zinc and chromium were detected in most of the samples, though most were within permissible limits. Continuous use of these products may result in an increase in the heavy metal levels in the ocular system and the human body. For human risk assessment, the estimated levels of Margin of Safety obtained for Cu and Pb in most cosmetic samples and Cr for powder samples showed values below 100% bio-accessibility, an indication that they are not safe for use. Presently, there are no regulations for allowable levels of heavy metals in cosmetics in used in Nigeria, hence, this study has created some awareness about the risk associated with use of some of the cosmetics especially through dermal exposure. Consequently, proper routine monitoring and most appropriate actions be taken by regulatory agencies in Nigeria to avert the prevalence of these heavy metals in cosmetic products is recommended.

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