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Concentration of Some Heavy Metals and Health Risk Assessment in Facial Cosmetic Products Found in Nigerian Markets

Yonma, O.V.; Akporhonor, E.E.; Agbaire, P.O. and Kpomah, B.

Department of Chemistry, Delta State University, Abraka, Nigeria.

ABSTRACT

The levels and health risk assessment of some toxic metals (Cd, Pb, Cr, Ni, Zn, Fe and Mn) in different facial cosmetic products sold in different markets in Delta State, Nigeria were assessed. Purchased samples were digested with concentrated HNO_3, H_2SO_4 and $HClO_4$ (1:2:2 v/v), and analysed for toxic metals levels using atomic absorption spectrometry. The concentration (mg/kg) obtained were as follows: facial toner: Pb (1.41±1.03), Cd (0.03±0.01), Mn (5.85±1.61), Fe (1.69±0.53), Ni (0.12±0.12), Zn (0.12±0.06) and Cr (0.33±0.32); facial moisturizer: Pb (2.17±0.75), Cd (0,21±0.005), Mn (0.76±0.08), Fe (5.13±2.76), Zn (0,24±0.03), Ni (0.00±0.00), Cr (0.00±0.00); and facial foundations: Pb (2.21±1.13), Cd (0.23±0.02), Mn (42.666±25.90), Fe (835.05±130), Zn (1.08±0.36), Ni (0.08±0.08), Cr (0.00±0.00). The concentration in the samples follow the order Cd<Ni<Zn<Cr<Pb<Fe<Mn for facial toner Ni<Cr<Cd<Zn<Mn<Pb<Fe for facial moisturizer and Cr<Ni<Cd<Zn<Pb<Mn<Fe for facial foundations. Systemic exposure dosage revealed that all metals were less than 3% of their provisional tolerable daily intake. Pb and Cd exert little risk in the facial cosmetics assessed as their MoS values were less than 100. Mn also exert little risk in facial toner and foundation. Fe exerts high risk in facial foundation while other metals exert no risk associated with their occurrence in facial cosmetics.

Keywords: Facial toner, moisturizer, foundation, toxic metals, MoS

INTRODUCTION

A cosmetic product is any preparation or substance intended to be applied to the different external parts of the human body such as the epidermis, nails, hair system, external genital organs, lips or applied to the mucous membranes of the oral cavity or teeth with a view of cleaning, protection, perfuming, correcting body odours and changing their appearance (Oyedeji *et al.*, 2011). The different forms of cosmetic include lipstick, foundations, face moisturizers, powder, face toners and rouge (used to colour the face, removing flaws to produce an impression of health and lightening (Reed, 2007).

In recent times, the routine use of cosmetics products for care of the human body is on the increase. Apart from the high demand of availability of such cosmetic products, their associated health effects due to potential contamination by chemical substances have drawn the attention of researcher (Nnorom *et al*., 2005; Barakat, 2011). The continuous use of cosmetic products can result in the absorption of contaminants present in them. Dermal exposure is anticipated to be the most notable route for cosmetic products since cosmetics products are applied to the skin. Some cosmetic products may be accidentally ingested which may result in an obvious oral route of exposure to such chemical contaminants (Ramakant *et al*., 2014).

There is therefore the need for cosmetics products to be regularly monitored for toxic metals contents, in order to understand and minimize their effect on users, as well as guarantee their safety (Omolaoye *et al*., 2010; Samia *et al*., 2017). Due to the fact that there are data on the concentration of toxic metals in cosmetics and their negative impact with respect to the study area, This study is thus of great importance, as it will serve as a model scale to reveal the concentrations of toxic metals in some of cosmetic products available in Nigerian markets, as well as the potential health effects arising from long-term usage.

Materials and Methods

Study Area

Ten (10) different brands of face moisturizers, face toners and foundation totalling thirty (30) samples in all were purchased from markets in four (4) different towns in Delta State, Nigeria. These includes: Asaba, Warri, Ughelli and Udu.

Sample Digestion

All samples were digested according to the method described by Welz and Sperling (1999).

Liquid Samples

A digestion mixture was also made using 4 mL of perchloric acid, 8 mL of nitric acid and 8ml of sulphuric respectively, and was poured into an amber glass bottle. 100 mL of the liquid sample was measured into a 250 mL cornical flask and 5 mL of concentrated nitric acid was added to the 100 mL sample and it was placed in the fume cupboard and allowed to boil for about 15 - 20 minutes until white fume was noticed coming out of the beaker, the hot plate was turned off and the solution was allowed to cool and was filtered with funnel and filter paper into a clean 100 mL volumetric flask and was made up to 100 mL with distilled water , the solution was later transferred into an heavy metal sample bottle and was labelled appropriately with codes.

Solid Samples

1g each of the samples were weighed with a weighing balance into a 100 mL beaker, A digestion mixture was made using 4 mL of perchloric acid, 8 mL of nitric acid and 8 ml of sulphuric acid respectively, and was poured into an amber glass bottle. The samples was labelled boldly, 5 mL of concentrated nitric acid was added to the sample and it was placed in the fume cupboard and allowed to boil for about 15 – 20 minutes until white fume was noticed coming out of the beaker, the hot plate was turned off and the solution was allowed to cool and was filtered with funnel and filter paper into a clean 100 mL volumetric flask and was made up to 100 mL with distilled water ,the solution was later transferred into an heavy metal sample bottle and was labelled appropriately with codes.

Analysis of Samples for Metal Concentration

The most frequently used analytical method for the analysis of heavy metal contamination in most cosmetic products is the Atomic Absorption Spectroscopy (AAS) and this method was applied in this study. According to Adepoju-Bello *et al.*, (2012), the calibration plot method was used for the analysis, and for each element, the instrument was autozeroed using the blank (Ultra Pure water) after which the standard was aspirated into the flame from the lowest to the highest concentration. The corresponding absorbance was then be obtained by the instrument and the graph of absorbance against concentration was plotted. The samples was then analysed in duplicates with the concentration of the metals present being displayed in parts per million (ppm) by the instrument after extrapolation from the standard curve (Adepoju-Bello *et al.*, 2012),

Health Risk Assessment

The Margin of Safety (MoS), a measure of uncertainty, can be used to estimate the danger of human exposure to metallic contaminants in various facial cosmetic products. The MoS is calculated as the ratio of the estimated Systemic Exposure Dosage (SED) to the cosmetic ingredients lowest no observed adverse effect level (NOAEL).

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

The systemic availability of a cosmetic substance is estimated by taking into consideration the amount of the finished product applied to the skin per day, the concentration of metals in the cosmetic product under study, the dermal absorption of the metal and a human body weight value

The systemic exposure dosage (SED) is given by the formula:

$$SED(\mu g\ kg^{-1}\ bw\ day^{-1}) = \frac{C_S \times AA \times SSA \times F \times RF \times BF}{BW} \times 10^{-3}$$

Where

Cs is the concentration of metal in the facial cosmetic product ($mgkg^{-1}$) and

AA is the amount of facial cosmetic product applied per day. The estimated daily amounts (in g) applied was 0.51. SSA is the skin surface area onto which the products are applied. The applied surface area (in cm2) for the different facial cosmetic products was 563.

RF is the retention factor (1.0); F is the frequency of application per day;

BF is the bioaccessibility factor; 10^{-3} is the unit conversion factor; and

BW is the body weight (kg). A default body weight of 60 kg was used in this study.

The values of AA, SSA, and RF used in this study were the standard values established by the Scientific Committee on Consumer Safety (SCCS).

For the studied metals, the NOAEL values were calculated by using the relationship,

NOAEL = RFD × UF × MF

Where

UF and MF are the uncertainty factor (reflecting the overall confidence in the various data sets) and the modifying factor (based on the scientific judgment used) respectively.

In this case, the default values of UF and MF were 100 and 1.

The RFDs (in mg kg^{-1} day^{-1}) used were Pb (4×10^{-3}), Cd (1×10^{-3}), Cr (3×10^{-3}), Co (3×10^{-4}), (Zn (3.0×10^{-1}), Fe (7.0×10^{-1}), Cu (4.0×10^{-2}), Mn (1.4×10^{-1}), and Ni (2×10^{-2}).

Statistical Analysis

SPSS (v23) was used for summary statistics. Past (v3) was used to check the level of significance of different metals. Where there is significant difference, the data is further subjected to Duncan Multiple Range Test (DMRT) and Tukey to determine the difference within and between the groups.

Results and Discussion

The result of the metals in the facial toner, facial moisturizer and facial foundation is presented in Table 1. Pb and Cr shows no significant different in facial moisturizers and foundations. However, Pb is significantly lower in facial toner than facial moisturizer and facial foundation. Cd, Mn, Fe, Zn and Ni are statistically different among the different facial cosmetics evaluated.

Table 1: Heavy metals in facial toner, moisturizer and foundation

Metals (mg/kg)	Pb	Cd	Mn	Fe	Zn	Ni	Cr
Facial toner	1.41± 1.03^{a}	0.03± 0.01^{a}	5.85± 1.61^{a}	1.69± 0.53^{a}	0.12± 0.06^{a}	0.12± 0.12^{a}	0.33± 0.32^{a}
Moisturizer	2.17± 0.75^{b}	0.21±. 0.05^{b}	0.76± 0.08^{b}	5.13± 2.76^{b}	0.24± 0.03^{b}	<0.001± 0.00^{b}	<0.001± 0.00^{b}
Foundation	2.21± 1.13^{b}	0.23± 0.02^{c}	42.67± 25.90^{c}	835.05± 130.36^{c}	1.08± 0.36^{c}	0.08± 0.08^{c}	<0.001± 0.00^{b}
p-value	0.04	0	0.01	0	0.01	0.01	0.01
WHO (2011)	10	3	NP	30	25	0.2	0.55

Mean with the same superscript on the same column are not significantly different at p = 0.05

Lead (Pb)

The concentration of Lead ranged from 0.01-10.00 mg/kg and for facial toner, 0.00 – 5.71 mg/kg in facial moisturizer and from 0.00 –7.80 mg/kg in facial foundation. The mean concentrations of the Lead in the assessed cosmetics in this study were within WHO (2011) permissible limit as presented in Table 1.

Karri *et al.* (2016) noted Lead as neurotoxic, nephrotoxic, and hepatotoxic when it comes into contact with important organs, and it may also have effects on the reproductive system. According to Attard and Attard (2021), it is a possible carcinogen to humans and has been found that consumers who use eye cosmetics have three times the amount of Pb in their blood than non-consumers. The highest concentration of Lead was observed in 25.5 % facial moisturizer cosmetics, while the lowest concentration was found in 0.2 5% facial foundation. This result agrees with the study of Iwegbue *et al*. (2015) who reported Pb of <0.03 – 107 mg/kg in their study. The maximum Lead concentration in this study (10 mg/kg) however was lower than the 22.57 mg/kg reported by Nasirudeen and Amaechi (2015). The concentration of Pb varied significantly ($p<0.05$) between the different groups of facial cosmetics except for facial moisturizer and facial foundation ($p>0.05$). Since lead accumulates in the body over time, lead containing cosmetics whether applied a number of times a day or on daily basis can contribute to significant lead exposure levels. Lead absorbed through the skin may be eliminated via sweat and other extracellular fluids and hence not be as great a health hazard as ingested lead.

Cadmium (Cd)

The concentration of Cd ranged from <0.001 – 0.09 mg/kg and for facial toner, 0.001–5.71 mg/kg in facial moisturizer and from 0.14 – 0.41 mg/kg in facial foundation. The concentrations of the Cd in the assessed cosmetics in this study were within WHO (2011) permissible limit. The highest concentration of Cd was observed in facial moisturizer cosmetics. In the facial toner, it was the lowest percentage (0.31%) of overall metals. The highest concentration (2.47 %) was however observed in facial moisturizer. The lowest concentration of Cadmium of this study is similar to the <0.02 reported by Iwegbue *et al*. (2015) but the maximum concentration of Cd in this study is lower than the 17.75 mm/kg they reported. The concentration of Cd varies significantly ($p<0.05$) between the different groups of facial cosmetics. This is in contradiction with the report of Nasirudeen and Amaechi (2015) who reported higher limit in 67 % of Cadmium in the cosmetics examined while assessing the heavy metals in some cosmetics in Kaduna.

Cd is a metal that has been used in cosmetics because of its colourful salts, which range from deep yellow to orange, according to Safavi *et al.* (2019). It has been related to a variety of toxicities in humans, particularly as a result of its absorption after topical application of various cosmetics (Alam *et al.,* 2019). When administered topically, it can cause irritating dermatitis. It is a significant source of concern because it tends to accumulate in human tissues before gradually releasing into the general circulation (Ahmadi-Jouibari *et al.,* 2017). Systemically, the skeletal, reproductive, metabolic, respiratory, and renal systems are the most affected. It's been related to renal illness, diabetes, lung cancer, and osteoporosis, among other things. It also produces oxidative stress, which hastens the skin's aging process (Chavatte *et al.,* 2020).

Manganese (Mn)

The concentration of Mn in facial toner ranged from 0.50 – 14.41 mg/kg and 0.28 – 1.17 mg/kg in facial moisturizer while in in facial foundation, it ranged from 0.18–266.96 mg/kg. From the result obtained from the evaluation of Manganese in facial cosmetics in Delta State, the highest concentration of Manganese (266.96 mg/kg) was observed in facial foundation. Of all metals, the Manganese percentage is 61.26 %, 8.93 % and 4.84 % in facial toner, moisturizer and foundation respectively. Manganese is the highest heavy metal concentration in facial toner with 61.26% in comparison to all other metals. The mean concentration of Mn in facial moisturizer is similar to that (0.47-1.97 mm/kg) reported by Okoro *et al.* (2015). However, the mean concentration of facial toner and facial foundation of Mn determined in this study is far higher than that which was reported by Okoro *et al.* (2015). The concentration of Mn varies significantly ($p<0.05$) between the different groups of facial cosmetics. The high concentrations of Mn in the facial cosmetics may due to uncontrollable or intentional addition of inorganic pigments into the cosmetics by the manufacturers.

Iron (Fe)

The concentration of Fe ranged from 0.08 – 4.44 mg/kg and for facial toner, 0.006 – 29.72 mg/kg in facial moisturizer and from 122.33 –1610 mg/kg in facial foundation. The concentrations of the Fe in the assessed cosmetics in this study were within WHO (2011) permissible limit except 835.05 mg/kg in foundation which was above 30 mg/kg permissible limit by WHO (2011)**.** The highest concentration of Fe (1610 mg/kg) was observed in facial foundation. Fe concentration is the highest among all heavy metals in facial foundation as it takes 94.74 % of the total metals this cosmetic. This is in correlation with the findings of Okoro *et al.* (2015). The concentration of Fe varies significantly ($p<0.05$) between the different groups of facial cosmetics.

Zinc (Zn)

The concentration of Zn ranged from 0.00 – 0.68 mg/kg and for facial toner, 0.06 – 0.40 mg/kg in facial moisturizer and from 0.33–3.99 mg/kg in facial foundation. The concentrations of the Zn in the assessed cosmetics in this study were within WHO (2011) permissible limit. The highest concentration of Zn (3.99 mg/kg) was observed in facial foundation cosmetic. The range of Zinc of this study is lower than 2.33 –3.01 mg/kg reported by Okoro *et al.* (2015). It is also lower than 18 – 320 mg/kg reported by Iwegbue *et al.* (2019). Given that toxic heavy metals are known to accumulate in the biological system over time and to cause diseases like cancer or skin issues, it is clear from the current study that using some cosmetic products exposes consumers to low concentrations of these dangerous metals, which could be risky for their health.

Nickel (Ni)

The concentration of Ni ranged from <0.001 – 1.17 mg/kg and for facial toner, 0.00 – <0.001 mg/kg in facial moisturizer and from <0.001 – 0.82 mg/kg in facial foundation. The concentrations of the Ni in the assessed cosmetics in this study were within WHO (2011) permissible limit. The highest concentration of Nickel (1.17 mg/kg) was observed in facial toner cosmetic. In the facial moisturizer evaluated, Nickel was totally absent. In all the facial cosmetics evaluated, the highest concentration of Nickel (1.26 %) was however observed in facial toner. The concentration of Ni varies significantly ($p<0.05$) between the different groups of facial cosmetics. It is noted by Maurpawar (2015), Nickel is one of the metal contaminants that are unavoidably present in a variety of natural components used in cosmetic goods. Nickel is considered a contact allergen that can cause skin sensitization, allergies, and dermatitis through direct and frequently protracted exposure. Nickel allergy has been diagnosed in people as a result of its presence in topical cosmetic items and jewellery. Nickel can also harm the respiratory system, leading to nasal and lung cancer (Brandao *et al.,* 2012; Halicz *et al.,* 2015).

Chromium (Cr)

The concentrations of Chromium in facial toner ranged from 0.001 – 3.29 mg/kg and 0.01 – 0.01 mg/kg in facial moisturizer while the concentrations of Cr in facial foundation ranged from 0.001 – 0.001 mg/kg. From the result obtained from the evaluation of Cr in facial cosmetics in Delta State, the highest concentration of Cr (3.29 mg/kg) was observed in facial toner cosmetic. Of all metals, the Cr percentage is 3.46 %, 0.00 % and 0.001 % in facial toner, moisturizer and foundation respectively. This is lower than the report (9.1–44.4 mm/kg) of Iwegbue *et al.* (2016) in their evaluation of concentrations and exposure of risks of some metals in facial cosmetics in Nigeria. The concentration of Cr varies significantly ($p<0.05$) between the different groups of facial cosmetics. Based on the mean Concentrations, the concentrations of heavy metals are arranged in descending order as follow; Mn> Fe >Pb> Cr > Zn > Ni > Cd for facial toner while Fe > Pb > Mn > Zn > Cd > Cr > Ni for facial moisturizer and Fe >Mn>Pb> Zn > Cd > Ni > Cr for facial foundation. . Face moisturizer has higher level of Fe than permissible limit by WHO (2011).

Table 2: Systemic exposure dosage of metals in facial cosmetic products obtained

Metals (mg/kg)	Pb	Cd	Mn	Fe	Zn	Ni	Cr
Syetemic Exposure Dosage							
Facial toner	9.45×10^{-2}	2.00×10^{-3}	3.92×10^{-1}	1.13×10^{-1}	8.00×10^{-3}	8.00×10^{-3}	2.21×10^{-2}
Moisturizer	1.45×10^{-1}	1.40×10^{-2}	5.09×10^{-2}	3.43×10^{-1}	1.61×10^{-2}	6.70×10^{-5}	6.70×10^{-5}
Foundation	1.48×10^{-1}	1.54×10^{-2}	0.29×10^{1}	5.59×10^{1}	7.23×10^{-2}	8.53×10^{-2}	6.70×10^{-5}

Table 3: Margin of Safety of metals in facial cosmetic products obtained

Metals (mg/kg)	Pb	Cd	Mn	Fe	Zn	Ni	Cr
Facial toner	0.42×10^{1}	5.00×10^{1}	3.57×10^{1}	6.18×10^{2}	3.75×10^{3}	2.50×10^{2}	1.43×10^{2}
Moisturizer	0.28×10^{1}	0.71×10^{1}	2.75×10^{2}	2.04×10^{2}	1.86×10^{3}	2.98×10^{4}	4.47×10^{3}
Foundation	0.27×10^{1}	0.65×10^{1}	0.49×10^{1}	0.12×10^{1}	4.15×10^{2}	2.34×10^{1}	4.47×10^{3}

The estimated SED (mg kg^{-1} day^{-1}) and MoS of metals from the use of these facial cosmetic products are presented in Table 2 and Table 3 respectively. The SED of Pb from the use of these facial cosmetic products ranged from 9.45×10^{-2} to 1.48×10^{-1} mg kg^{-1} bw day^{-1}. Despite the fact that the existing provisional tolerable daily intake (PTDI) for Pb was withdrawn by the FAO/WHO joint committee we nevertheless used the PTDI value of 3.6 mg kg^{-1} bw day^{-1} as an indicator for comparison with the results of the estimated daily intake. The estimated SED of Pb from the use of these facial cosmetic products was below the PTDI (The Provisional Tolerable Daily Intake) value. The PTDI of Cd is set at 1mg kg^{-1} bw day^{-1}; however, the European Food Safety Authority (EFSA) set the provisional tolerable weekly intake (PTWI) of Cd as 2.5 mg kg^{-1} bw $week^{-1}$. The SED values of Cd from the use of these facial cosmetic products which ranged from 2.00×10^{-3} to 1.54×10^{-2} constituted less than 2 % of the EFSA provisional tolerable intake. The SED of Mn from the use of these facial cosmetic products ranged from 5.09×10^{-2} to 0.29×10^{1} mg kg^{-1} bw day^{-1}. This is also below the 10 mg kg^{-1} bw day^{-1}. The SED of Mn in all the cosmetics was less than 1% of PTDI. The estimated SED values of Fe obtained from the use of these facial cosmetic products ranged between 1.13×10^{-1} and 5.59×10^{-1} mg kg^{-1} bw day^{-1}, while the SED of Zn ranged between 8.00×10^{-3} and 7.23×10^{-2} mg kg^{-1} bw day^{-1}. The recommended daily intakes (RDI) of Fe and Zn are set at 12.5 and 12 mg per day respectively. The estimated SEDs of Fe and Zn from application of these facial cosmetic products are below their respective recommended intake values. The SED of Fe and Zn in all the cosmetics was less than 1% of PTDI. The estimated SED values of Ni and Cr obtained from the use of these facial cosmetic products ranged between 6.70×10^{-5} to 8.53×10^{-2} mg kg^{-1} bw day^{-1} and 6.70×10^{-5} and 2.21×10^{-2} mg kg^{-1} bw day^{-1} respectively. The tolerable daily intakes of Ni and Cr are 700 mg kg^{-1} bw day^{-1} and 200 mg kg^{-1} bw day^{-1} respectively.

The margin of safety values obtained in this study indicated that some metals exert little risk in relation to their occurrence in the facial cosmetics. Pb and Cd exert little risk in the facial cosmetics assessed as their MoS values were less than 100. Mn also exerts little risk in Facial toner and foundation. Fe exert high risk in facial foundation while every other metals exert no risk associated with their occurrence in facial cosmetics

Conclusion

The system exposure dosage revealed that all metals were less than 3% of their provisional tolerable daily intake. Pb and Cd exert little risk in the facial cosmetics assessed as their MoS values were less than 100. Mn also exerts little risk in Facial toner and foundation. Fe exerts high risk in facial foundation while every other metal exert no risk associated with their occurrence in facial cosmetics. Excessive quantities of both essential and nonessential metals can sometimes lead to toxicity; this may possibly be caused by metabolic deficiency. Both acute and chronic exposure can be treated by chelation therapy; this therapy requires the hard-soft-acid-base relationship in choosing the chelating agent. The effect of chelation on the toxicity of heavy metals and chelating agents was reported by (Kpomah *et al.*, 2016). Their research showed a decrease in the toxicity of their complexes as compared to the uncoordinated ligand and the central metal ion. On chelation, the polarity of the metal ion is reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups (Kpomah and Kpomah, 2017).

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