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International Digital Organization for Scientific Research
IDOSR JOURNAL OF COMPUTER AND APPLIED SCIENCES 3(1):12-24, 2018. ISSN: 2579-0803

Determination of Heavy Metal Contents in Eyeliners, Lipsticks and Black Tattoo Inks (Local and Foreign) Sold In Adamawa State

[1]Salau I.O., [2]Maitera O.N., and [3]Hassan I.

[1,2]Department of Chemistry, Modibbo Adama University of Technology, Yola, Adamawa State, Nigeria.

[3]Department of Chemical Science Technology, Federal Polytechnic, mubi, Adamawa State,Nigeria.
Email; idrisalau@yahoo.co.uk

ABSTRACT

Cosmetics use is very popular all over the world some of these make-up substances such as henna is part of the culture and traditions of some locals and so they are being used since very young ages. This makes detection of toxic contents in cosmetics marketed in Adamawa State of crucial importance. This particular study was aimed at determining the concentration of some toxic substances in make-up items (local and foreign) sold in Adamawa State, Nigeria. Sixteen different make-up items were analyzed for seven heavy metals. Atomic Adsorption Spectrophotometry (AAS) was used to quantify the presence of these heavy metals after acid digestion. The results of the heavy metal analysis indicated that the concentrations of Cd, Co, Cr, Cu, Ni, Pb, and Zn were found to be in the range of 0.01 – 0.03 ppm, 0.5 – 2.0 ppm, 0.16 – 0.48 ppm, ND – 8.5 ppm, 0.52 - 2.85 ppm, ND - 0.3 ppm and 0.39 – 5.73 ppm, respectively. These values (except that of Cr and Ni) were below the given EPA Guidelines for Tattoo and Permanent Make-up Substances (EPA, 2012). Coefficient of variation (CV) showed great variations in the concentrations of heavy metals in the products hence the uneven distribution of the metals. Prolonged use of some of these products may pose human health and environmental risks due to toxic substances loading through dermal contact and accumulation over a period of time.

Keywords:- cosmetics, heavy metals, para-phenyenediamine, polycyclic aromatic hydrocarbons.

INTRODUCTION

Right from time immemorial, cosmetics of one form or another have been used by humans to beautify themselves as they have great impact on history, fashion, culture and even lives of people. The use of cosmetics is widespread among females, though an increasing number of males are gradually using cosmetics in order to enhance their physical appearances. Cosmetics or makeup, as often called, are substances or preparations used to enhance the beauty of the human body apart from simple face cleaning. The different forms of cosmetics find different applications such as: tattoos which could be a temporary or permanent dermal marking; lipsticks and lip glosses used to colour the lips; foundation, concealer, powder and rouge used to colour the face, lightening and removing flaws to produce an impression of health and youthfulness; mascara used

to enhance the eyelashes; while eyeliners and eye shadow are used to colour the eyelids; nail polish used to colour the fingernails or toenails; creams and lotions usually clean the face and body, unclog the pores, enable proper perspiration and keeps the skin safe from acne, pimples or blemish. More than just enhancing beauty, Actors uses specialized forms of cosmetics too to change physical appearances [1].

Cheap brands of lipsticks and eye shadows imported from countries with poor safety, regulatory and manufacturing practice but sold in riyal stores in Saudi Arabian were analyzed. Lead was found with the range 0.27-3760 ppm for lipsticks and 0.42-58.7 ppm for eye shadow [2]. [3] stated that heavy metals are not listed as ingredients in some cosmetics due to lack of manufacturer testing or regulatory oversight. It is possible that the companies are not even aware that the products are contaminated and these contaminants likely get into the products when poor quality ingredients are used. Inadequate purification of the raw materials could also be a factor [4]. [5] and [6] in their separate works, reported that some of these heavy metals have been used as cosmetics ingredients in the past. Examples include preservative thimerosal (mercury), the progressive hair dye lead acetate and a number of tattoos pigments such as red cinnabar (mercuric sulphide).

Clinical observations, case reports and surveys show that a variety of adverse skin reactions or even health problems are associated with the use of some of these products[3]. This makes detection of toxic contents in some cosmetics marketed in Adamawa State of crucial importance. Hence, this research assesses the levels of lead, cadmium, copper, cobalt, chromium, nickel, and zinc in four different categories of make-up substances (i.e., black tattoo inks, lipsticks, henna and eyeliners) commonly available and used in Adamawa State, Nigeria, in order to find out if they comply with maximum concentrations of heavy metals and other constituents in the New Zealand's Environmental Protection Authority (EPA)'s Guidelines for Tattoo and Permanent Make-up Substances [7] which might have the potential to be harmful for humans.

MATERIALS AND METHODS

Sample collection, preparation and analysis

A total of 16 samples comprising of different types of lipsticks, eyeliners, local and foreign black tattoo inks was purchased from superstores and open markets across Adamawa State, Nigeria. The samples were labelled accordingly.

All glassware and plastic containers to be used were washed with liquid soap, rinsed with water, soaked in 10% v/v nitric acid for 24hrs, cleaned thoroughly with distilled water and dried in such a manner to ensure that any contamination does not occur.

Concentrated nitric acid (10 ml) was added to 1 g of the sample in a 100 ml beaker and was heated on a hot plate at 95°C for 15 min. The digest was allowed to cool and 5 ml of concentrated nitric acid added and heated for additional 30 min at 95°C. The last step repeated (i.e. addition of 5 ml concentrated HNO_3) and the solution was then reduced to about 5 ml without boiling. The sample was cooled again and 2 ml of deionized water and 3 ml of 30% hydrogen peroxide were added. With the beaker covered, the sample was heated gently to start the peroxide reaction. When effervescence became excessively vigorous, the sample

was removed from the hot plate and 30% hydrogen peroxide added in 1 ml increments, followed by gentle heating until the effervescence subsides. Concentrated hydrochloric acid (5 ml) and 10 m l of de-ionized water were added and the sample heated for additional 15 min without boiling. The sample was then cooled and filtered through a Whatman No. 42 filter paper and diluted to 50 ml with deionized water [8].The concentration of cadmium, cobalt, chromium, copper, lead, nickel and zinc were determined using Atomic Absorption Spectrophotometer. The analysis was done in triplicate and Coefficient of Variation (CV) was used to show the distribution patterns of the heavy metals in the samples.

Recovery studies

The method of standard addition which is considered as a validation method [9] was used to demonstrate the validity of our method. Hence, a recovery test was performed using method of standard addition. Standard solutions containing Cd, Co, Cr, Cu, Ni, Pb and Zn were prepared and spiked with digested samples after dilution of sample to 50 ml.

RESULTS AND DISCUSSION

Concentration of cadmium in the samples

The range of cadmium mean concentrations in the four categories of samples were 0.01 -0.03 ppm in henna while the range in the lipsticks, eyeliners and foreign black tattoo inks is the same (0.02 – 0.03 ppm). The results obtained in this study were compared with the available international permissible limits as there are no national guidelines on metals in cosmetics in Nigeria. The values obtained in this study which were below the permissible limit of 0.2 ppm by the Environmental Protection Authority, indicates the samples are safe of any Cd toxicity. Skin absorption of Cd is rare [10] but when absorbed into the body, cadmium accumulates in the kidney and the liver. Although cadmium can be found in almost all adult tissues, the total amount absorbed by humans has been estimated to be between 0.2–0.5 µg/day, with absorption via skin estimated to be 0.5% [11]. Cadmium and cadmium compounds are considered to be carcinogenic to humans by the IARC and are also classified as known human carcinogens by the United States Department of Health and Human Services.

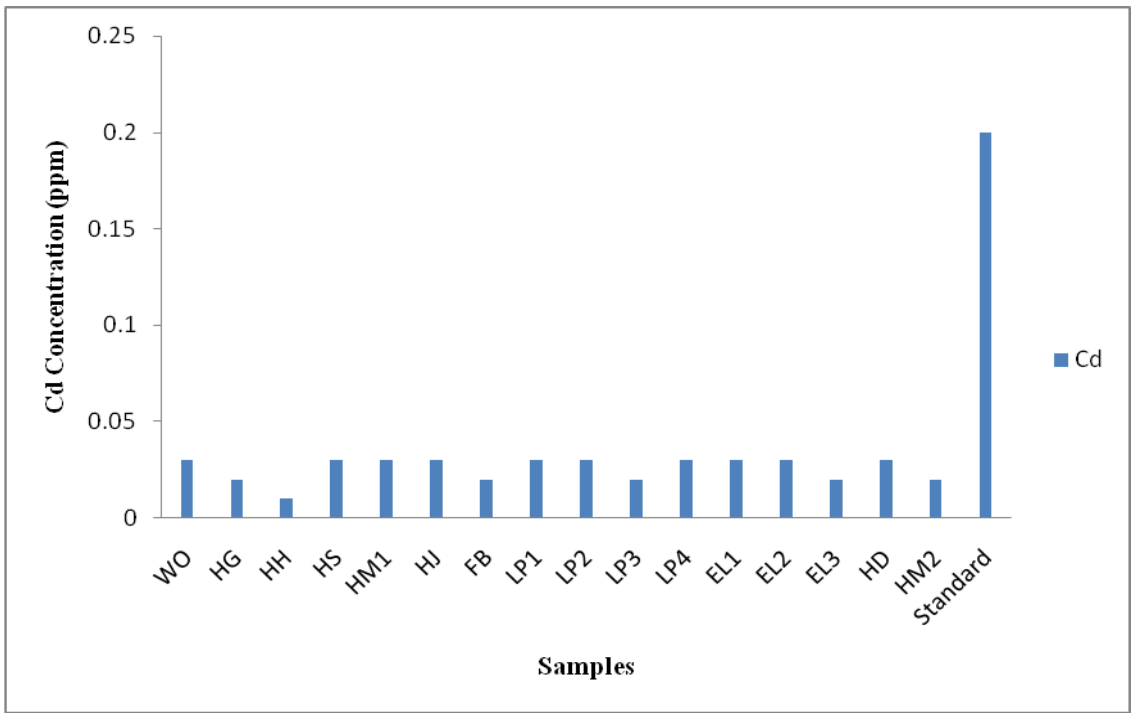

Figure 1:The mean concentration (ppm) of cadmium in all the samples

Concentration of cobalt in the samples

The mean concentrations of Cobalt in the samples ranged from 0.9 – 2.0 ppm in henna, 0.7 – 1.6 ppm in lipsticks, 0.5 – 1.7 ppm in eyeliners and 1.1 – 1.4 ppm in foreign black tattoo inks. The results of the present study as seen in Figure 2 indicated that these samples of cosmetic products contained Co at concentrations below the suggested safe limit of 25 ppm by EPA's guidelines for maximum concentrations of heavy metals in tattoos and permanent makes up substances [7] for greater health protection.

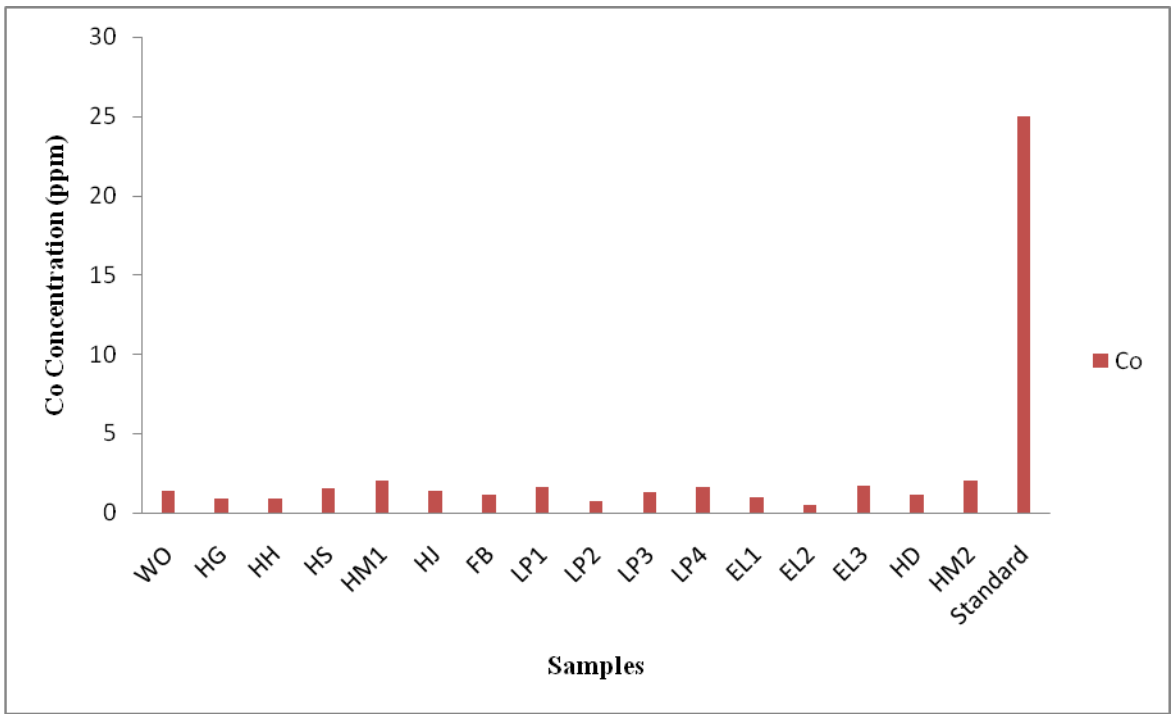

Figure 2:The mean concentration (ppm) of cobalt in all the samples

Concentration of chromium in the samples

The concentrations of Chromium in the samples ranged from 0.21 – 0.48 ppm in henna, 0.21 – 0.42 ppm in lipsticks, 0.16 – 0.42 ppm in eyeliners and 0.38 – 0.41 ppm in foreign black tattoo inks. Figure 3 shows that concentrations of Cr observed in all the samples were higher than the 0.2 ppm EPA's guidelines for maximum concentration of heavy metals in tattoos and permanent make up substances [7] except for eyeliner (EL1).The higher concentrations of Cr found in some of the samples could be due to the use of Cr-containing colouring agents. For example, chromium hydroxide green ($Cr(OH)_3$) and chromium oxide green ($Cr_2O_3.2H_2O$) are colouring agents used in cosmetic products. These colourants contain chromium (III) which causes skin allergies through percutaneous absorption through the skin. Eye shadow is an example of a cosmetic product in which significant amounts of colourants are used [8]. Chromium in the +III and +VI oxidation states is a potential hapten in the development of contact allergy [12].

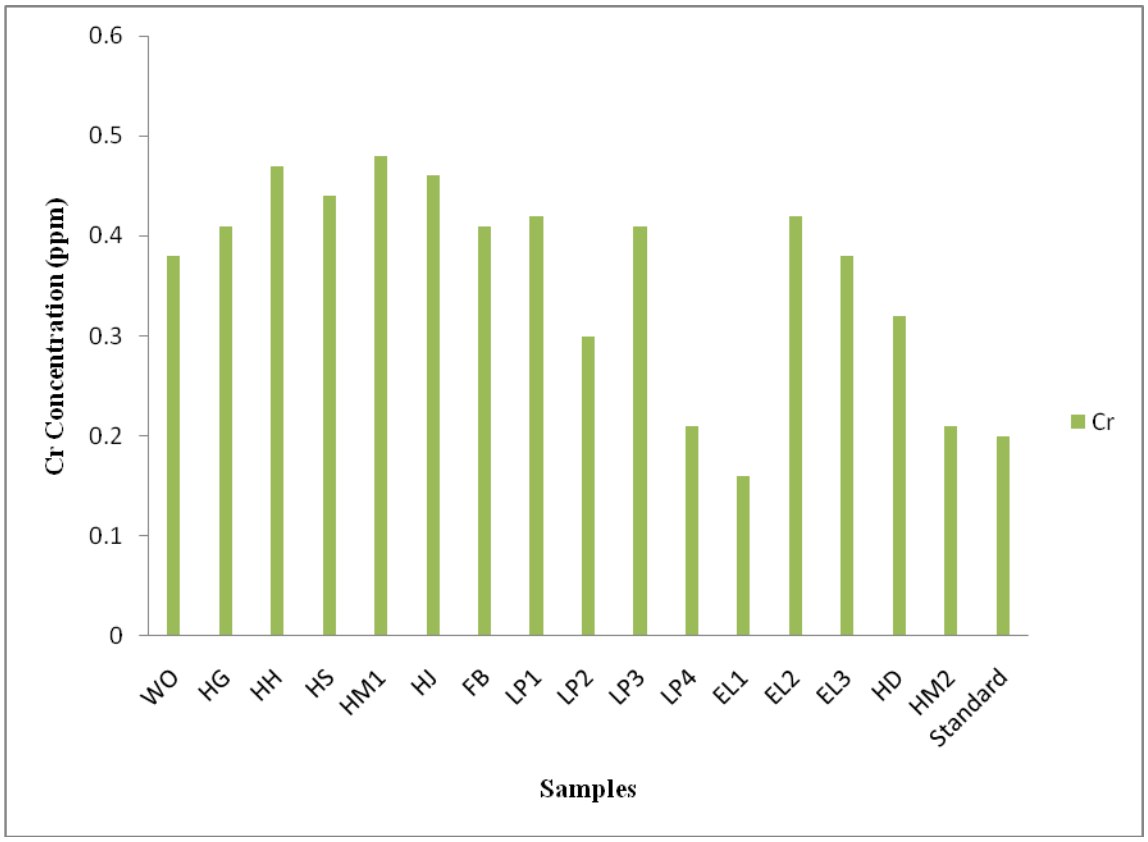

Figure 3:The mean concentration (ppm) of chromium in all the samples

Concentration of copper in the samples

The concentrations of Cu in the samples ranged from 0.10 – 0.30 ppm in henna, ND – 8.50 ppm in lipsticks, ND – 1.90 ppm in eyeliners and no Cu was detected in the foreign black tattoo inks. The highest mean concentration observed was in Lp1 while there was no detection of Cu in WO, FB, Lp2 and Lp4. Figure 4 shows that all the samples analysed had Cu concentrations less than 25 ppm which is the EPA's guidelines for maximum concentrations of heavy metals in tattoos and permanent makeup substances [7]. High concentration of Cu in Lp1 could be due to the fact that copper-containing compounds might have been used as pigments in that type of facial cosmetics.

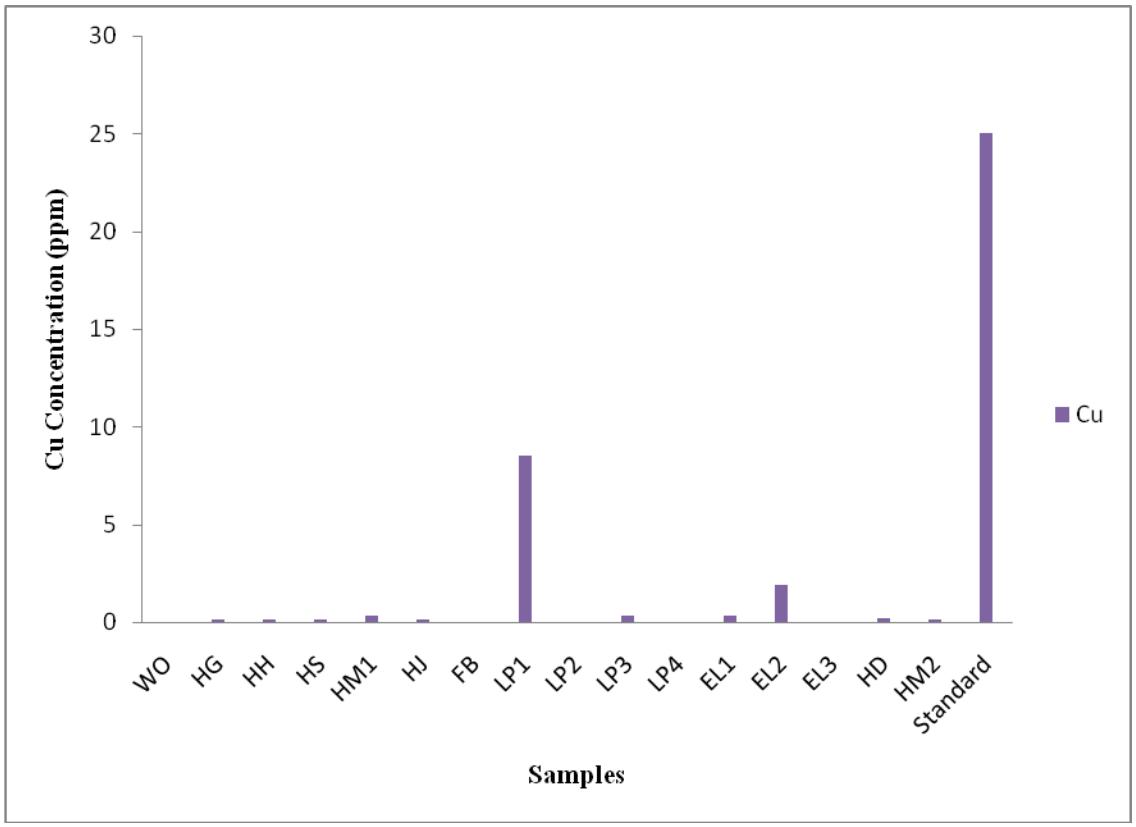

Figure 4:The mean concentration (ppm) of copper in all the samples

Concentration of nickel in the samples

Nickel mean concentrations in the henna ranged from 0.46 – 2.85 ppm, 0.52 – 0.83 ppm in the lipsticks, 0.65 – 0.74 ppm in the eyeliners and 0.60 – 0.78 ppm in the foreign black tattoo inks. When the results were compared with the 0.2 ppm of EPA's guidelines for nickel, values in all the samples were above the permissible limit as shown in Figure 5 and hence likely to cause health risk to the consumers from dermal exposure.Nickel is naturally occurring element and may be an essential element in humans. Fetal exposures can occur, which can be passed to breast-feeding infants [13]. High levels of exposure can lead to health effects depending on the route and the kind of nickel exposed to [14]. Nickel represents the main cause of contact dermatitis and minimal amount of other toxic metals can trigger pre-existing allergy. Nickel dermatitis produces erythema, eczema and lichenification of the hands and other areas of the skin that is in contact with nickel [15].

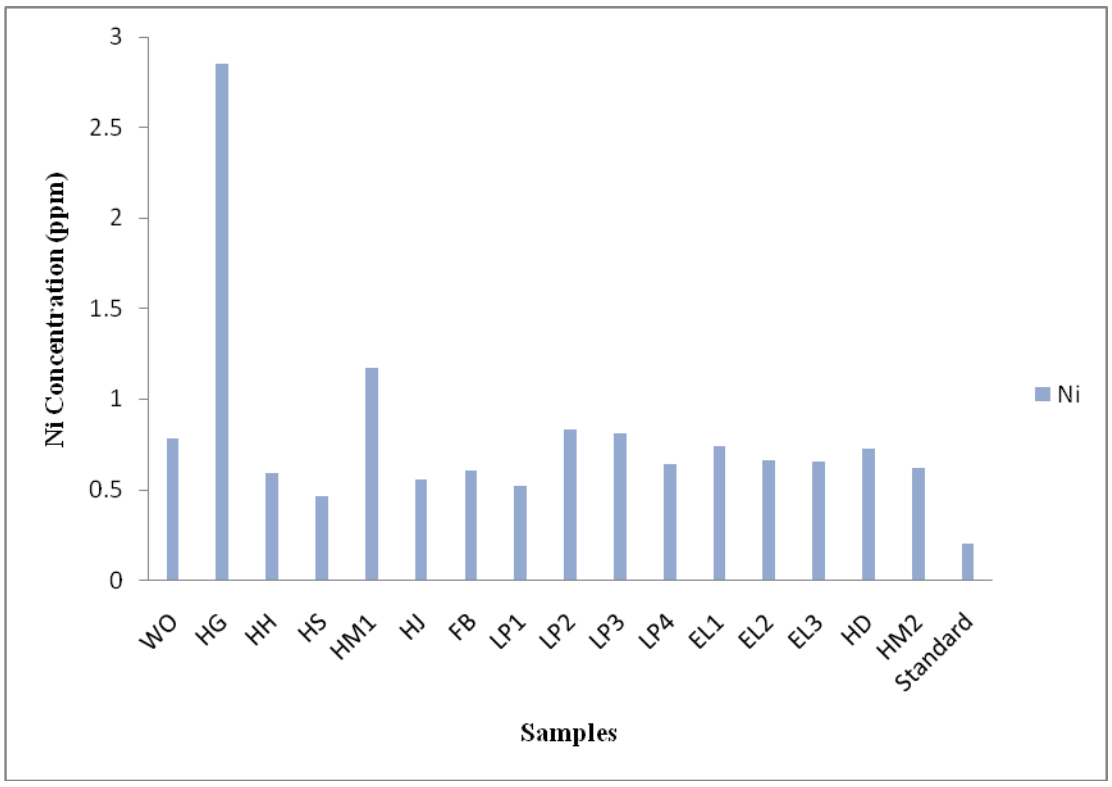

Figure 5:The mean concentration (ppm) of nickel in all the samples

Concentration of lead in the samples

The mean concentrations of lead in the samples ranged from 0.1 – 0.3 ppm in henna, 0.1 – 0.3 ppm in lipsticks, 0.2 – 0.3 ppm in eyeliners and ND – 0.3 ppm in foreign black tattoo inks. The results obtained were compared with the available international limits of 2 ppm in cosmetics by the Environmental Protection Authority (EPA)'s guideline for maximum concentrations of heavy metals in tattoos and permanent make-up substances [7] as seen in Figure 6. 100%, of the henna, lipsticks, eyeliners and foreign black tattoo inks considered in this study were below the permissible limit, thus they are unlikely to pose any risk to the consumer through dermal exposure.Lead is a neurotoxin that is found in cosmetics, plastics, batteries, gasoline, insecticides, pottery glaze, soldered pipes, and paints [16].

IQ deficits have been associated with both low and high blood lead levels. Lead exposure has also been linked to miscarriage, hormonal changes, reduced fertility in men and women, menstrual irregularities, delays in puberty onset in girls, memory loss, mood swings; nerve, joint and muscle disorders; cardiovascular, skeletal, kidney and renal problems [17]. Lead and inorganic lead compounds have been classified as possible and probable carcinogens to humans [18]

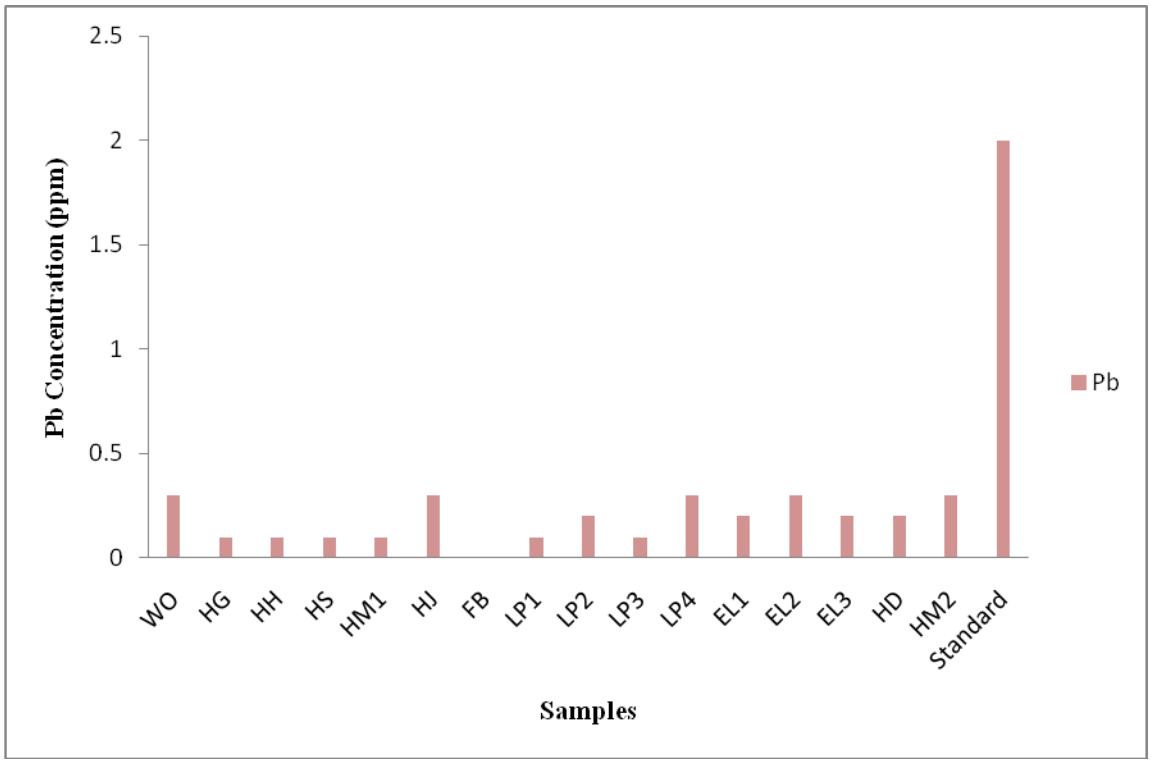

Figure 6:The mean concentration (ppm) of lead in all the samples

Concentration of zinc in the samples

The range of zinc mean concentrations were 1.23 - 5.35 ppm, 0.79-3.51 ppm 0.39-5.73 ppm and 1.95-3.18 ppm in the henna, lipsticks, eyeliners and foreign black tattoo inks respectively. Among the samples under study, sample EL2 (eyeliner) and HM2 (henna) had high concentrations of zinc (5.73 and 5.35 ppm respectively) which were far below the standard (50ppm) by Environmental Protection Authority for Zn as seen in Figure 7, thus they are unlikely to pose any risk to the consumer through dermal exposure. However, accumulation over time is likely to have negative impacts on humans. Some of the human health effects associated with zinc exposure includes inhibition of oxygen and calcium transportation in the body; inhibition of nerve transmission in the brain, reduced IQ and learning disabilities, intra-uterine fatal death, premature delivery and low birth weight. In the workplace environment, zinc contamination can lead to a flu-like condition known as metal fever. This condition will pass after two days and is caused by over sensitivity. Zinc can pose a danger to unborn and newborn which may be exposed through mother's blood or milk [19].

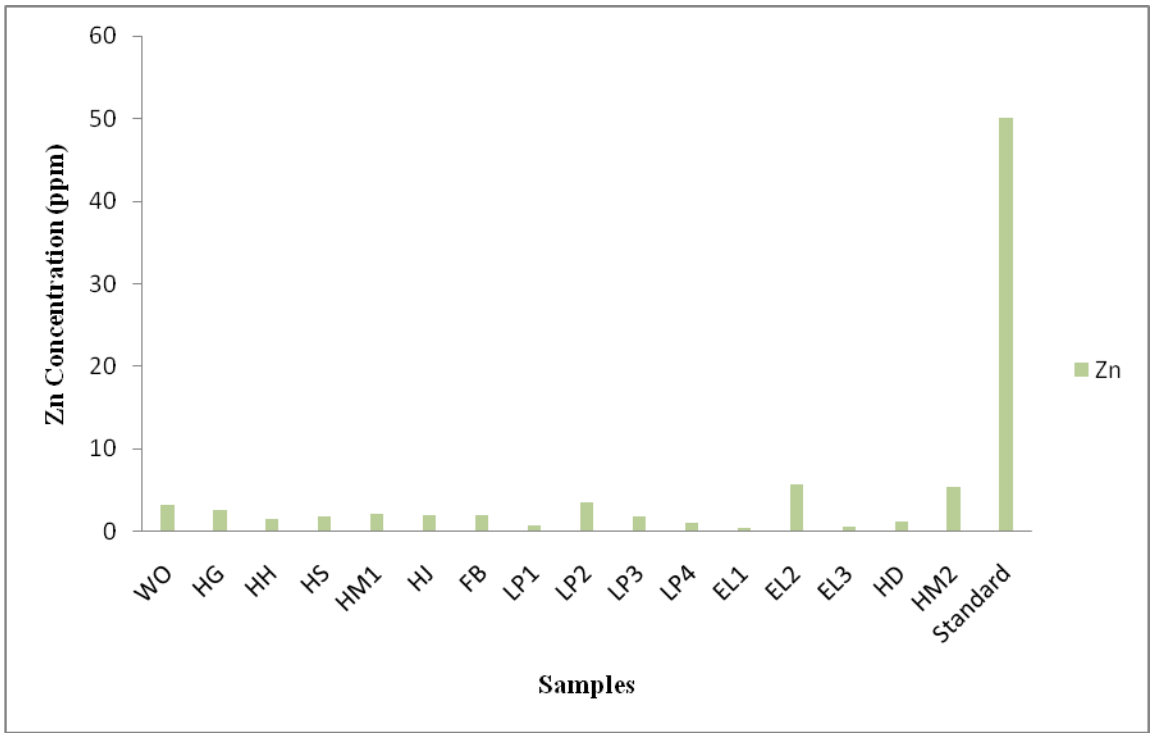

Figure 7: The mean concentration (ppm) of zinc in all the samples

Statistical analysis of the heavy metals.

The coefficient of variation (CV) was used to explain the distribution patterns of heavy metals in the four different classes of cosmetics (Henna, lipsticks, eyeliners and foreign black tattoo inks) commonly used in Adamawa state. The higher the CV values, the greater the uneven distributions of the parameters under consideration [20]. Thus, in the henna, the CV values ranged from 23.1% in Cr to 79.2% in Ni, and 15.7 in Cd to 165.4 in Cu in the Lipsticks, 7.2 in Ni to 139.3 in Cu in the eyeliners and not detected (ND) in Cu to 141.4 in Pb in the foreign black tattoo inks (Table 1). These showed that there are no guidelines or strict regulations in the use of different raw materials in the production of some of these cosmetics. There were great variations in the concentrations of heavy metals in the products hence the uneven distribution of the metals.

Table 1: Comparison of the mean concentrations (ppm), standard deviation (SD) and Coefficient of variation (CV) of heavy metals in the different products.

Metals	Henna (n=7)	Lipstick (n=4)	Eyeliners (n=3)	Foreign black tattoo ink (n=2)
Cd	0.024±0.007(29.2%)	0.028±0.004(15.7%)	0.027±0.006(22.2%)	0.025±0.007 (28%)
Co	1.4±0.434(31%)	1.3±0.367(28.2%)	1.067±0.603(56.5%)	1.25±0.212(17%)
Cr	0.399±0.092(23.1%)	0.335±0.086(25.7%)	0.32±0.14(43.8%)	0.395±0.021(5.4%)
Cu	0.143±0.073(51%)	2.2±3.639(165.4%)	0.733±1.021(139.3%)	ND
Ni	0.994±0.787(79.2%)	0.7±0.128(18.2%)	0.683±0.049(7.2%)	0.69±0.127(18.4%)
Pb	0.171±0.088(51.4%)	0.175±0.083(47.4%)	0.233±0.058(24.9%)	0.15±0.212(141.4%)
Zn	2.406±1.278(53.1%)	1.82±1.052(57.8%)	2.253±3.013(133.7%)	2.565±0.87(33.9%)

Based on the mean heavy metal concentrations in this study, the decreasing order of metals in the four categories of sample in this study are as follows;

Henna: Zn > Co > Ni > Cr > Pb > Cu > Cd.
Lipsticks: Cu > Zn > Co > Ni > Cr > Pb > Cd.
Eyeliners: Zn > Co > Cu > Ni > Cr > Pb > Cd.
Foreign black tattoo inks: Zn > Co > Ni > Cr > Pb > Cd > Cu.

Recovery study of heavy metals and validation

In order to ascertain the efficiency of the analytical results, recovery study was carried out for Cd, Co, Cr, Cu, Ni, Pb, and Zn in some of the samples (EL3, Lp3, HJ, EL2, HM2, HD and WO). This was achieved by spiking the samples with known concentrations of pure standards. The spiked samples were then passed through the analytical procedure and analysed to determine the concentrations of the metals (Table 2).The analytical method based on Flame Atomic Absorption Spectrophotometry (FAAS) provided good accuracy in the range 82.3 – 102.6% which indicates the absence of interferences.

Table 2: Recovery studies for trace elements and heavy metals

Metal	Base value (ppm)	Quantity added (ppm)	Quantity found (ppm)	Recovery (%)
Cd	0.02±0.36	1.0	1.018	99.8
Co	1.3±0.021	0.3	1.547	82.3
Cr	0.46±0.024	0.2	0.672	106
Cu	1.9±0.029	3.0	4.898	99.9
Ni	0.62±0.119	2.0	2.519	94.9
Pb	0.2±0.035	0.5	0.732	102.6
Zn	3.18±0.024	2.0	5.08	95

CONCLUSION

In some of the products, the levels of the metals were higher than the available permissible limits and reported studies. The metal concentrations in the samples were in the order: henna > eyeliners > foreign black tattoo inks > lipsticks. Prolonged use of cosmetic products may result in an increase in the heavy metal levels in the human body and so the use of some of these cosmetic products may be considered as a source of toxic metal poisoning. Though, the metals are from the contamination of raw materials and use of sub-standard raw materials, lack of compliance by small scale manufacturers, and lack of strict regulations. Currently, there are no national regulations and permissible limits of heavy metals and other toxins in most consumer products including cosmetic products in Nigeria. These findings call for instant mandatory regular testing programs to check for the presence and concentration of heavy metals/toxic substances in cosmetic products that are imported to Nigeria and sold in Adamawa State in order to limit the excess amount of toxic substances and hence protect the consumers' health. Further efforts are needed to enlighten the users and the general public on the dangers of using unknown/misbranded products that are pumped in large quantities to many markets in Nigeria.

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