EVALUATION OF HEAVY METALS IN SOME COSMETIC PRODUCTS IN LAGOS NIGERIA.

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ABSTRACT

The harmful effects of hidden hazardous heavy metals in cosmetics are not well emphasized in Nigeria. These metals are known to be of toxic effects to human according to the results of several studies. This study was aimed at evaluating the presence of heavy metals like: Arsenic (As), Cadmium (Cd), Chromium (Cr), lead (Pb), Nickel (Ni), Mercury (Hg) and Zinc (Zn) in selected cosmetics. Thirty samples of imported cosmetics classified as: Nail polish (Np), Eye shadow (Es), Perfume (Pf), Body spray (Bs), Lipstick (Ls) and Powder (Pd) were purchased from three major markets (Balogun, Idumota and Ojota markets) in Lagos State, Nigeria. Samples of these cosmetics were prepared and analyzed for the various concentrations of the metals present using flame atomic absorption spectrometer. The results obtained showed the presence of these metals in the analyzed cosmetics at varying concentrations. The ranges of the concentrations obtained for As, Cd, Cr, Pb, Ni, Hg and Zn were: 0.50 – 2.40 ppm, 0.20 – 6.10 ppm, 0.80 – 5.80 ppm, 0.20 - 3.20 ppm, 1.10 – 12.20 ppm, 0.10 – 1.80 ppm and 7.20 – 19.60 ppm respectively. The peak concentrations respectively detected for As, Cd, Cr, Pb, Ni, Hg and Zn, were: 2.40 ppm in Pd-27, 6.10 ppm in Ls-15, 5.80 ppm in Es-6, 3.20 ppm in Ls-12, 12.20 ppm in Np-3, 1.80 ppm in Pd-27 and 19.60 ppm in Pd-26. Obtained concentrations for this study were relatively higher compared with similar studies carried out in the European axis. Our results suggest that dermal exposure to heavy metals through the use of cosmetics is the major route of exposure to these metals. Users of cosmetics should avoid excessive use of it since these metals could pose hazardous health effects on them.

Keywords: Heavy metals, Impurities, Bioaccumulation, cosmetics and Dermal exposure.

INTRODUCTION

Heavy metals refer to any metallic element that has a relatively high density and is toxic or poisonous even at low concentrations (Lenntech, 2014). They are found naturally in the environment in rocks, water and soils. Therefore, they exist in the manufacture of pigments and can be used in trace quantities into raw materials used in the manufacture of the various cosmetic products available to users. Some of these metals are used in cosmetics for one reason or the other, for example Cadmium's (a deep yellow to orange element) colour properties enables it to be used in some lipsticks and facial cosmetics, thiomerasl (mercury) as a preservative, the progressive hair dye lead acetate and a number of tattoo pigments such as red cinnabar (mercuric sulfide) and so on. Apart from the regulated intentional uses of these heavy metals in cosmetics, they can be found as impurities also in various cosmetic products. The latter makes it very difficult to avoid exposure to heavy metals because of their prevalence nature in the environment (Nnorom *et al.*, 2005; Ayenimo *et al*., 2010; USEPA, 2013; Health Canada, 2011; Rashed *et al*., 2010).

Several researches have related the causes of some health issues to the presence of heavy metals such as arsenic, mercury, lead, cadmium, chromium, etc as impurities in cosmetics, (Darbre, 2001 and 2003; Health Canada, 2011; Harvey and Darbre, 2004; McGrath, 2003; Houston, 2007; Kawata *et al*., 2007; Liu *et al*., 2009; IARC, 2010). Adepoju-Bello *et al.,* (2012) reported that cosmetics expose users to low level concentrations of toxic heavy metals may pose potential health

issues to the users since heavy metals are known to accumulate in the biological system over time and also known to induce skin problems such as cancer. Heavy metals such as lead and cadmium are notable for their ability to accumulate in the body tissue faster than the body detoxification pathways can get rid of them; thus, a gradual build up of toxic levels which can greatly be enhanced through the application of cosmetics and other personal care products on the skin. The skin, despite being a protective barrier, some components of cosmetics such as arsenic, cadmium and lead penetrate and become available in our systems, (Health Canada, 2009). Loretz *et al.,* (2006), found that the possibility of exposure to cosmetic products may occur when applied via spray, while dermally applied products to the mucous membranes present the possibility of enhanced availability or in the case of lips products provide the opportunity for oral ingestion. Nnorom *et al.* (2005), reported the significant levels of heavy metals in facial cosmetics such as eye pencil and lipsticks.

Heavy metals in cosmetics have been shown to have adverse effects on human health. Lead has been described as the environment's most harmful contaminant to arise in human civilization and has been shown to impair renal, hemopoietic and nervous system with different reports linking it to deficiency in cognitive functioning (Chukwuma, 1997; Nnorom *et al.,* 2005). Lead poisoning leads to poor intelligent quotient (IQ) (Wang *et al.,* 2002); inhibition of the synthesis of haemoglobin, dysfunctions in kidneys, joints, reproduction and vascular systems (Ogwuegbu and Muhanga, 2005). Al-Saleh *et al.,* (2009), linked lead poisoning to infertility and miscarriage. High concentrations of zinc can result in stomach cramps, vomiting, skin irritation, anaemia and nausea (Odukudu *et al.,* 2014).

International agency for Research on Cancer (IARC) 2010, reported that cadmium and its compounds are considered human carcinogens. It is extremely toxic even at low concentrations. Nickel though a trace elements required in the body in minute quantities, can accumulate in the kidneys, bones and thyroid and cause toxicity (Rashed *et al.,* 2010). Allergy to nickel is common and it can cause severe contact dermatitis (Health Canada, 2010). IARC (2010), arsenic and its inorganic compounds are considered to be carcinogenic to humans. Chromium (VI) ion (Cr^{6+}) is a known human carcinogen; inhalation causes lung cancer (Agency for Toxic Substances and Disease Registry (ATSDR), 2008). Mercury is a neurotoxin and the prolonged use of products containing it can lead to inflammation of the liver, kidneys and urinary track infection, (Ramakant *et al.,* 2014). Mercury is particularly hazardous during foetal development and it is readily absorbed by the skin. Neither mercury nor thiomerasl are highly common as direct ingredients or impurities, but its high toxicity means that the presence of mercury in any cosmetics is of concern (Adepoju-Bello *et al.,* 2012).

Arsenic, cadmium, lead and mercury are among the metals banned as intentional ingredients in Canada. The aim of this study was to determine the concentrations of As, Cd, Cr, Pb, Hg, Ni and Zn in commonly used cosmetics available in Lagos State, Nigeria and to assess if the concentrations are within the acceptable standards.

MATERIALS AND METHODS

The modified method of Umar and Caleb, (2013) together with Hydride Generation/Cold Vapor Atomic Absorption Spectroscopy was used for Arsenic and Mercury in this work.

Collection of Samples

Thirty different cosmetics in the classes of nail polish (1-5), eye shadow (6-10), lipstick (11-15), perfume (16-20), body spray (21-25) and powder (26-30) were bought from Balogun, Idumota and Ojota markets, Lagos State, Nigeria. The cosmetics were coded as shown in Table 1.

Table 1: Samples list and their codes

Samples Code	Samples Brand	Samples Code	Samples Brand
Np-1	Colodion gel 3.2.1	Es-6	Black Opal
Np-2	Viva	Es-7	Iman
Np-3	Everyone	Es-8	Romantic
Np-4	Vienne	Es-9	My Colour
Np-5	Liz	Es-10	Ushas
Pf-16	Seduction	Lp-11	Island Beauty Blue Flame
Pf-17	Professional	Lp-12	Mary-Kay
Pf-18	Nauveaute	Lp-13	Romantic
Pf-19	Nikita	Lp-14	Iman
Pf-20	Wishbone	Lp-15	Miss Rose
Bs-21	One love	Pd-26	Iman
Bs-22	Cool breeze	Pd -27	Black Opal
Bs-23	Treajar	Pd-28	Classic
Bs-24	Wishbone	Pd-29	Bouquet
Bs-25	Balila	Pd-30	Fashion Faire

Preparation of Standard Solutions

Analytical grade tri-oxo-nitrate (v) acid (65% sigma Aldrich) and Tetra-oxo-chloric (VII) acid (70% Sigma Aldrich) were used for samples preparation. Calibration standards for each heavy metal were prepared each day from the certified standard stock solution (1000 ppm manufactured under ISO 9001 quality Assurance System Perkin Elmer) in the range of 0.5 to 10 ppm. All solutions were prepared in double distilled water. Dilution correction was applied for samples diluted or concentrated during analysis.

Preparation of Samples

The solid samples were crushed in a porcelain mortar. 2g of each sample was weighed using analytical balance and then taken into a 100 ml digestion flask. 10 ml of Tri-oxo nitrate (V) acid (HNO_3) was added and the flask was placed in the dark over night. On the next day, 5 ml of Tetra-oxo-chloric (VII) acid ($HClO_4$) was added to it. The mixture was then placed on a hot plate at 50°C for 15 minutes and then the temperature was raised slowly up to 200°C. Heating was continued until the white fumes of the $HClO_4$ disappeared. This was done on a digester inside the fume cupboard. After the digestion, the contents were cooled and filtered through the Whatman filter paper (№ 2). Then the samples were transferred to the 50 ml volumetric flask and diluted with de-ionized distilled water up to the mark. A solution of each sample was taken into sample bottles for analysis.

A Perkin Elmer Analyst 200 Atomic Spectrometer equipped with hollow cathode lamp was used for the analysis while Hydride Generation/Cold Vapor Atomic Absorption Spectroscopy was used for As and Hg. The instrumental parameters were adjusted as specified by the manufacturer. The hollow cathode lamps for the selected metals were of wavelengths and slit wavelengths respectively as: Ni- 232.00nm ; 0.20nm, Cd- 228.80nm ; 0.70nm, Cr- 357.90nm ; 0.70nm, Zn- 213.90nm ; 0.70nm, Pb- 283.30nm ; 0.70nm, As- 193.70nm ; 0.70nm and Hg- 253.70nm ; 0.70nm. Limit of Detection (LOD) of AAS used was 0.0001ppm. The gas used was acetylene with 20Pa pressure and air 45Pa pressure. The instrument was calibrated with standard solutions and the samples were introduced to it.

RESULT AND DISCUSSION

The samples were analyzed and the concentration of the metals present were displayed in parts per million (ppm) on the display unit of the spectrometer and were presented in Table 2, as follows,

Table 2: Concentrations of Heavy Metals in Analysed Cosmetics Samples

Sample Codes	As (ppm)	Cd (ppm)	Cr (ppm)	Pb (ppm)	Ni (ppm)	Hg (ppm)	Zn (ppm)
Np-1	1.00	1.80	1.20	ND	ND	1.20	13.60
Np-2	0.80	2.10	2.30	1.30	**1.10**	1.20	
Np-3	**0.50**	ND	ND	ND	**12.20**	1.60	9.40
Np-4	0.70	4.00	3.80	1.80	2.70	1.10	
Np-5	0.80	2.40	2.60	1.90	3.00	0.40	
Es-6	1.10	ND	**5.80**	1.80	4.80	0.70	7.80
Es-7	1.00	2.00	3.10	1.30	1.90	**0.10**	
Es-8	1.00	1.20	3.20	ND	7.80	0.60	**7.20**
Es-9	1.10	1.90	2.30	1.20	2.90	0.50	
Es-10	1.20	2.10	5.20	0.90	2.10	1.10	
Ls-11	1.20	1.80	2.80	ND	ND	0.80	8.80
Ls-12	0.70	3.60	2.00	**3.20**	ND	0.30	10.80
Ls-13	0.90	5.90	3.10	2.00	2.00	0.10	
Ls-14	1.00	3.80	1.40	2.10	1.90	0.30	
Ls-15	1.20	**6.10**	1.30	2.00	2.70	1.00	
Pf-16	1.90	3.60	1.90	1.90	1.90	1.00	
Pf-17	1.90	2.10	1.10	1.90	2.90	1.20	
Pf-18	1.80	2.00	3.80	1.70	2.00	0.90	
Pf-19	1.10	ND	**0.80**	1.80	ND	0.90	11.80
Pf-20	1.20	ND	1.20	ND	ND	0.80	12.80
Bs-21	1.00	2.20	3.80	2.00	4.00	1.00	
Bs-22	1.90	**0.20**	2.20	**0.20**	7.20	1.30	
Bs-23	2.10	1.20	2.00	ND	2.00	0.70	
Bs-24	2.00	3.30	4.00	1.80	2.60	0.50	
Bs-25	1.80	2.80	2.90	1.90	1.80	1.10	
Pd-26	1.80	ND	1.80	ND	4.80	1.20	**19.60**
Pd-27	**2.40**	4.20	1.80	2.20	1.50	1.80	
Pd-28	1.70	2.50	1.10	1.40	1.80	0.80	
Pd-29	1.40	3.60	1.60	1.60	3.10	1.20	
Pd-30	1.60	3.10	2.00	1.50	3.60	1.00	

ND= Not Detected

Table 3: Mean, Standard Deviation and Range of Each Heavy Metal Analyzed in all the Cosmetics in ppm

Heavy Metals	Mean (ppm) ± SD	Range (ppm)
As	1.33 ± 0.40	0.76 – 1.78
Cd	2.75 ± 0.84	1.80 – 4.24
Cr	2.49 ± 0.78	1.66 – 3.92
Pb	1.74 ± 0.39	1.30 – 2.53
Ni	3.27 ± 0.90	1.30 – 2.53
Hg	0.88 ± 0.25	0.50 – 1.20
Zn	13.03 ± 4.22	9.80 – 19.60

The results of the analysis indicated the uneven distribution of the metals and their concentrations. The highest concentration of Zn was found in sample Pd-26 (19.60 ppm), Ni in sample Np-3 (12.20 ppm), Cd in sample Ls-15 (6.10 ppm), Cr in sample Es-6 (5.80 ppm), Pb in sample Ls-12 (3.20 ppm), As in sample Pd-27 (2.40 ppm) and Hg in sample Pd-27 (1.80 ppm). The mean concentration of the heavy metals for all the cosmetics analyzed in decreasing order were 13.03ppm

for Zn, 3.27ppm for Ni, 2.75ppm for Cd, 2.49ppm for Cr, 1.74ppm for Pb, 1.33ppm for As and 0.88ppm for Hg. Table 4, shows the distribution of the metals in the various cosmetics considered.

Table 4: Mean concentration of heavy metals in the cosmetic products.

Forms of Cosmetics	As (ppm)	Cd(ppm)	Cr(ppm)	Pb(ppm)	Ni(ppm)	Hg(ppm)	Zn(ppm)
	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
Nail polish	0.76±0.16	2.58±0.85	2.48±0.93	1.67±0.26	4.75±4.36	1.10±0.39	11.50±2.10
Eye shadow	1.08±0.07	1.80±0.35	3.92±1.34	1.30±0.32	3.90±2.20	0.60±0.32	7.50±0.30
Lipstick	1.00±0.19	4.24±1.60	2.12±0.72	2.53±0.51	2.20±0.36	0.50±0.34	9.80±1.00
Perfume	1.58±0.35	2.57±0.73	1.76±1.08	1.83±0.08	2.27±0.45	0.96±0.14	12.30±0.50
Body spray	1.76±0.40	1.94±1.12	2.98±0.81	1.45±0.74	3.52±2.00	0.92±0.29	17.50±1.70
Powder	1.78±0.34	3.35±0.63	1.66±0.31	1.68±0.31	2.96±1.21	1.20±0.33	19.60±0.00

The highest concentration of Zn in this study was 19.60 ppm in sample Pd-26, this value was greater than a concentration of 0.332 ppm reported by Odukudu *et al.*, (2014). This may be adduced to the shinning nature of Zinc, this may tempt manufacturers to add either regulated or unregulated amount of it in the various samples.

Cd highest was 6.10 ppm in sample Ls-15, this was higher than the impurity level of 3 ppm obtained in a similar research reported by Health Canada (2009). The value obtained for Cd in this work exceeded the limits suggested by Nnorom *et al.*, (2005) of 1ppm, and 0.50 ppm by Gondal *et al.*, (2010). Ni highest concentration was found in sample Np-3, as 12.20 ppm, this level was below the safety permissible level of 1701µg/g (Basketter, 2003) and 5 ppm, (Gondal *et al.*, 2010). The value 3.20 ppm for Pb in sample Ls-12 was lesser than the recommended safety level of 10 ppm (Health Canada, 2009) but higher than 1 ppm (Gesund und Wirtschaftlicher, 2010), 0.2 ppm (Expert Panel, 2007) and 0.5 ppm (Gondal *et al.*, 2010). Environmental Defence Canada (EDC), (2011) suggested a safety level of 3 ppm for As. The highest concentration of As in this study was 2.40 ppm in sample Pd-27 which was below the safety level of EDC, (2011). EDC, (2011) also recommended a safe value of 3 ppm for Hg and the highest concentration for Hg for this study was found to be 1.80 ppm in sample Pd-27 indicating that it was lower. Chromium's highest concentration was 5.80 ppm in sample Es-6, although not further varrified if it was found as Cr^{6+}. This value was higher than the permissible level of 0.00047 ppm for Cr^{6+} as reported by Odukudu *et al.*, (2014).

Comparing Heavy Metals in the analysed Cosmetics for this Study with Similar Study carried out by Umar and Caleb, (2013), there was significant difference in the concentrations of Cd. There where mark

differences in the concentration of Ni, Pb and Cr, these indicated that the concentrations of the impurities differs with manufacturers and locations.

Furthermore, our results indicated that the major route of heavy metals entrance into the body is through dermal exposure. With the continual use of the analyzed cosmetics, users are mostly exposed to five out of the seven metals evaluated through dermal applications i.e. Zn, Ni, Cr, As and Hg. The main source of exposure of Pb and Cd is through ingestion as depicted in Figure 1.

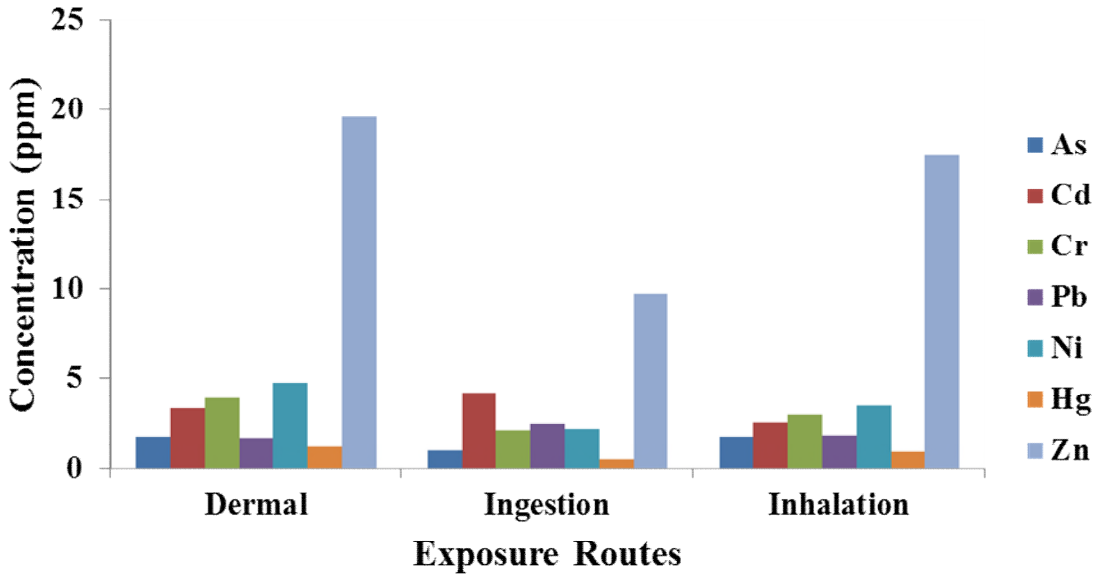

Figure 1: Routes of Heavy Metals Exposure in the Analysed Cosmetics

The study has shown notably the presence of As, Cd, Cr, Pb, Ni, Zn and Hg in cosmetics sold in Lagos state. These metals were contained in relatively high concentrations with respect to some safety limits reported. Therefore, their presence in cosmetics could act as additional source of heavy metals exposure. The possibilities of bioaccumulation in living tissues could be of potential harm to human health.

The concentrations of some of these metals are relatively high in this study with respect to their known toxicity on human health. Dermal exposure is the most significant route of entrance of these metals into the body. Therefore, users of these cosmetics are at high risk of the harmful effects of these heavy metals. For other contaminant detected that were below the permissible limit, continual use of such products may cause slow release of these metals into the human body and thus manifest their harmful effects as a result of bioaccumulation over a period of time.

CONCLUSION

The results obtained indicated that these metals were present in cosmetics in varying concentrations. Zn had the highest concentration for all the cosmetics samples analyzed with a concentration of 19.60 ppm and a mean concentration of 13.03 ppm. The highest concentration of each metal were: As– 2.40 ppm in sample Pd- 27, Cd– 6.10 ppm in sample Ls- 15 , Cr– 5.80 ppm in sample Es-6, Pb– 3.20 ppm in sample Ls -12, Ni– 12.20 ppm in sample Np-3, Hg– 1.80ppm in sample Pd- 27 and Zn– 19.60 ppm in sample Pd-26.

RECOMMENDATION

Most of these metals were present as impurities. Users should desist from indecent and excessive use of these cosmetics because of heavy metals “Add Up” and could result in long last harmful effects, Less is better. Natural beauty should be encourage and Artificial beauty jettison. Consumers are to choose safer products**.** Government can help pass smarter and health-protective laws. Ban

harmful and risky cosmetics, Demand that cosmetics companies fully disclose ingredients and support those that do.

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