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Full Length Research Article

SPECTROPHOTOMETRIC DETERMINATION OF HEAVY METALS IN COSMETICS SOURCED FROM KADUNA METROPOLIS, NIGERIA

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ABSTRACT
The concentrations of Pb, Cd, Hg and As in cosmetics sourced from Central, Barnawa and Kawo markets in Kaduna metropolis, in Nigeria were studied. After wet digestion, the samples were analysed using atomic absorption spectrophotometer – coupled with a hydride generator for As and CV-AAS for Hg. The mean concentrations observed in the cosmetic samples ranged between 5.93 to 22.57 mg/kg Pb; 0.12 to 1.11 mg/kg Cd; 30.00 to 90.32 mg/kg Hg; 0.11 to 1.0 mg/kg As. The results obtained revealed that Pb, Cd and Hg within each class of study were higher than the WHO permissible limits. However, it would be preterm to jump into conclusion to decide the fates of the analysed products on the bases of their heavy metal concentrations as the possibilities of counterfeiting or spuriousness of named brands cannot be overemphasized. An urgent need arises for strict regulations in Nigeria and concerted effort must be made to curb spuriousness of known brand and also in informing cosmetics users on the harmful effects of over consumption of cosmetics and heavy metal accumulations in the body.

Keywords: Cosmetics, Toxic heavy metals, AAS

INTRODUCTION

The word “cosmetic” is derived from the Greek word “kosmetikos” which means skilled in decoration”. Since the dawn of civilization, cosmetics have been utilized by people irrespective of their race, gender or age to beautify, modify or alter ones’ physical appearances. Cosmetics or makeup are substances or preparations used toenhance the beauty of the human body (Faruruwa and Bartholomew, 2014).

The general acceptance of cosmetics worldwide can be seen in the estimated sales by cosmetic industries in 2014, which is over 230 billion U.S dollars in total worth of sales in America, Europe, Australia, Asia and Africa (Romanowski, 2014). Most commonly used cosmetics in various parts of the world include facial make-up such as - lipsticks, lip glosses, foundations, concealers, powders, rouges, mascaras, eyeliners, eye shadows. Others include skin care creams, shampoos, hair dyes, deodorant and perfumes, nail polishes and mouth washes which find different application on different body parts.

The toxicity of product ingredients in various cosmetics is evaluated almost exclusively by a self-policing industry safety committee - the Cosmetic Ingredient Review (CIR). Researchers in the United States of America have shown that one in eight of the 82,000 ingredients used in personal care products are industrial care chemicals (St-Onge, 2012) which have been banned as intentional ingredients due to their plausible side effects. The continual patronage of cosmetics and the increasing views that the use of make-up, as cosmetics are colloquially known, does not necessarily make up beauty as asserted in the definition of the term has been an unaddressed issue. The above scenario prompted this study. This study aims at enlightening the public and users of make-up on the presence of any deleterious constituents present in these products, its grave consequences and its enormous economic implication. Also, this study would inculcate the need to use right doses of skin friendly products as the precise assessment of heavy metal concentration would narrow the margin between over consumption and adequate use of any cosmetic product.

Several researches have shown the presence of heavy metals in wide range of cosmetic products. Faruruwa and Bartholomew (2014) assessed heavy metals concentrations in facial cosmetic samples and reported varying abnormal concentrations of the metals; chromium (Cr), nickel (Ni), zinc (Zn) and iron (Fe). They established that the facial cosmetics analysed contained toxic metals and over exposure could lead to an increase in metal levels in the body beyond permissible limit.Furthermore, a study revealed mercury (Hg) in alarming levels ranging from 878 to 36,000ppm as recorded in six (6) out of sixteen (16) samples when Mexican skin lightening creams where analysed (Peregrinoet al., 2011) .Another study which specifically assessed heavy metals (Pb, Ni, Cu, Co, Cr, Mn, Zn, Cd) in some eye shadows imported from China into Nigeria reported the presence of these metals in varying concentrations (Omalaoyeet al., 2010).They reported that the obvious presence of these metals from the study indicated that these metals in facial cosmetics expose users to low levels of heavy metals. The study also showed that all the metals assessed except Chromium (Cr) where beyond permissible limits.Similar studies were carried out in New York and Hong Kong (Sin and Tsang, 2003; Mckelveyet al., 2010). In both studies, geometrical mean urine mercury (Hg) concentration identified a previously unrecognized source of exposure to inorganic mercury from the use of skin care products among residents. The urine mercury concentration was particularly high in residents that had used a beauty cream, within the last 45 days, before the experimental analysis.

However no known work has been done to investigate the presence of arsenic (As), mercury (Hg), cadmium (Cd) and lead (Pb) in samples such as lipsticks, eye liners, hair dyes and

powders sourced from Kaduna metropolis

MATERIALS AND METHODS

Sampling of the Cosmetics

Cosmetics samples of popular brands of lipsticks, eye liners, powders and hair dyes were collected from three different market locations – Central market, Barnawa market and Kawo market each representing key geographical location in Kaduna metropolis. Twelve samples, three of each mentioned products were purchased from open stores in these markets all within shelf life. Each samples obtained was labelled and physical analysis such as colour, manufacturing details, name of products, brand, batch number and ingredients listed on the labels of these products were noted. No two products possessed the same batch number. The samples were coded for easy identification as represented in Table 1.

Digestion of cosmetic samples

The digestion procedure employed for the elemental determination was as described by Mester (2003). For solid samples, 1.000 gram of sample was accurately measured into a conical flask and 15ml of concentrated nitric acid was added followed by 5ml 30% hydrogen peroxide and then 5ml concentrated HCl. The flask was closed for 15 minutes to ensure complete reaction thus beginning the first phase of acid wet digestion. The resulting mixtures were then heated at 150˚C 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 1 into a 100ml volumetric flask and diluted to volume using de-ionized water before aspiration into the instrument. Digestions were performed in triplicate to ensure accuracy and precision.

Heavy metal Analysis of Digested samples

The digested samples were then analyzed for the presence of Pb, Cd, Hg and As using an AAS (Thermo Fisher Scientific ICE 3000 AA).

Table 1: Samples sources and codes

Sample Name	Company Name on label	Country of Manufacture on label	Colour	Point of Sale	Code
Iman Lipstick	Iman	US	Red	CM	A
Iman Lipstick	Iman	US	Brown	KM	B
Jackelin Lipstick	Pantina	US	Purple	BM	C
Maybelline Powder	Maybelline	US	Brown	CM	D
Zikima Powder	Zikima	China	Brown	KM	E
Iman Powder	Zikima	US	Brown	BM	F
Cruset Hair Dye	Thai-Meko	Thailand	Black	CM	G
Black-N- Nature Hair Dye	Yucaitang	NS	Black	KM	H
Magic Hair Dye	Blue Diamond	Nigeria	Black	BM	I
Eyeliner kajal	Charming lady	China	Purple	CM	J
Eyeliner kajal	Charming Lady	China	Brown	KM	K
Eyeliner kajal	Charming Lady	China	Black	BM	L

RESULTS

The distributions of heavy metals in the analysed samples are presented in Table 2. The concentrations of Pb, Cd, As and Hg were observed in varying concentrations. The overall concentration mean concentration range of Pb in all analysed cosmetics varied between 5.93±0.01 to 22.57 ± 0.04 mg/kg (Table 3) with the highest concentration observed in sample E (Zikima powder) and the lowest observed in sample F (Iman powder). Detectable concentrations of Pb were found in 100% of the analysed samples. Based on the mean concentrations, the Pb contents in each group of samples were arranged as follows:

For Lipsticks; Sample C	>	Sample B	>	Sample A
For Powders; Sample E	>	Sample D	>	Sample F
For Eyeliners; Sample K	>	Sample L	>	Sample J
For Hair dyes; Sample G	>	Sample I	>	Sample H

The overall mean concentration range of Cd varied between 0.12 ±0.01 to 1.11 ± 0.04 mg/kg (Table 2) with the highest concentration observed in Sample J (Charming Lady eyeliner purple) and the lowest concentration observed in Sample C (Jackelin). Detectable

concentration of Cd was observed in 100% analyzed samples in which 67% showed concentration greater than the WHO permissible limits (See Table 3).The levels of Cd in the analyzed samples can be attributed to its usefulness as pigment (deep orange to yellow colouration) in the manufacture of some cosmetics.Based on the mean concentrations, the Cd contents in each group of samples were arranged as follows:

For Lipsticks; Sample A > Sample B > Sample C
For Powders; Sample E > Sample F > Sample D
For Eyeliners; Sample K > Sample L > Sample J
For Hair dyes; Sample H > Sample G > Sample I

The overall mean concentration range of Hg in all analysed cosmetics varied between 30.00 ± 0.69 to 90.32 ± 0.89 mg/kg (Table 2) with the highest concentration observed in sample I (Magic Hair dye) and the lowest observed in sample A (Iman red lipstick). Detectable concentrations of Hg were found in 100% of the analysed samples in alarming amounts. Based on the mean concentrations, the Hg contents in each group of samples were arranged as follows:

For Lipsticks; Sample C > Sample B > Sample A
For Powders; Sample E > Sample D > Sample F
For Eyeliners; Sample K > Sample J > Sample L
For Hair dyes; Sample I > Sample G > Sample H

Table 2: Mean levels of heavy metals in sampled cosmetics

Sample Code	Pb (mg/kg)	Cd (mg/kg)	Hg (mg/kg)	As (mg/kg)
WHO (Health Canada, 2007)	10	0.3	1	10
A	11.26Ψ ± 0.04	0.82 ± 0.06	30.00 ± 0.69	0.31 ± 0.01
B	6.35 ± 0.01	0.69 ± 0.09	71.60 ± 0.07	0.11 ± 0.01
C	18.21± 0.08	0.12±0.01	80.00±0.25	0.34±0.01
D	9.95± 0.07	1.10±0.06	57.45±0.36	0.21±0.01
E	22.57± 0.04	0.31±0.05	60.77±0.88	1.0±0.01
F	5.93± 0.03	0.32±0.07	48.99±0.96	0.12±0.02
G	18.60± 0.05	1.12±0.04	63.84±0.57	0.16±0.03
H	10.70± 0.08	0.42±0.01	53.74±0.58	0.27±0.01
I	14.53±0.01	0.76±0.08	90.32±0.89	0.81±0.08
J	7.80±0.02	1.11±0.04	47.28±0.54	0.07± 0.03
K	14.89±0.01	0.30±0.02	67.42±0.24	0.04± 0.02
L	11.61±0.05	0.38±0.05	42.63±0.75	0.50± 0.01

Ψ-Values in thetable are exressed as Mean ± S.E; n=12

Correlations studies among the heavy metals

Correlations among the metals as presented in Table 3 showed the interrelationship of the heavy metals in the analysed samples. Correlation study of the data indicated a relatively weak correlation between Pb and Cd (0.4995) and As and Hg (0.2508).

Table 3: Correlation studies of the concentration of the various heavy metals

Metals	Pb	Cd	Hg	As
Pb	1.0000Ψ	0.4995	-0.0381	- 0.1225
Cd	0.4995	1.0000	- 0.2088	-0.2964
Hg	-0.0381	- 0.2088	1.0000	0.2508
As	- 0.1225	-0.2964	0.2508	1.0000

Ψ- values are coefficient of correlation.

DISCUSSION

It would be worthwhile to know that maximum permissible concentration of heavy metals vary according to sub-population interest as children are moresusceptible to heavy metal poisoning than adults, the amount of product used and the site of application (Adepoju*et al.,* 2012 ; Health Canada, 2012). Symptoms of Pb poisoning include anaemia, sterility, learning impairment, behavioural abnormalities, decreased hearing (Nnorom*et al.,* 2005). Cd poisoningsymptoms ranges from renal and myocardicdysfunction, obstructive lung disease, bone defects (Duruibe*et al.,* 2007;Chauhan*et al.,* 2010). As poisoning include damage of tissues, organs, chromosomes, immune and urinary system (Sukenda*et al.,* 2012). Hg poisoning ranges from insomnia, dermal toxicity, nervousness, lack of coordination in taste, touch and sight (Sin and Tsang, 2003; Smith 2000).

Correlations among the metals as presented in Table 3 showed the interrelationship of the heavy metals in the analysed samples. Correlation study of the data indicated a relatively weak correlation between Pb and Cd (0.4995) and As and Hg (0.2508). The negative correlation observed in some of the metals shows that the metals are probably not from the same source and the presence of one does not necessarily indicate the presence of the other.

Conclusion

The results obtained in this study indicated the presence of heavy metals in cosmetics. All the analysed samples contained heavy metals; Pb, Cd, Hg and As in varying concentrations. Only As was within the permissible limits specified by WHO. However, it would be preterm to jump into conclusion to decide the fates of the named analysed products on the bases of their heavy metal concentration as the possibilities of spuriousness of these named brands cannot be over emphasized.

However, an urgent need arises for strict regulations in Nigeria and concerted effort must be made to curb spuriousness of known brand and also in informing make – up users on the harmful effects of heavy metal accumulations. This begs the question as to if a product can be tagged unfit by mere judging with respect to a standard of a particular regulatory body. Hence, there is need for unification of standard worldwide and the strict enforcement by authorities and compliance by manufacturers.Due to their ubiquitous nature, the absence or removal of heavy metals in cosmetic is impossible. However, if quality assurance chemists and process engineers are employed whose sole aim is to pin point possible source of contamination, the quality of these products can be improved as well as the health of users.Relevant authorities and manufacturers should rise up to the challenge of checkmating spurious products as this drags the name of reputable cosmetic manufacturing companies through the mud. Manufacturers should be made by regulatory authorities to specify the presence and concentration of carcinogenic and harmful heavy metals on their products. Further studies should be undertaken on assessing wide range of heavy metals in both synthetic and herbal cosmetics.

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