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Determination of Toxic Heavy Metals in Selected Cosmetics Samples Marketed in Ethiopia

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ABSTRACT

Nowadays people in the world are using various types of cosmetics for different purposes. Heavy metal impurities are common in cosmetic products due to their natural abundance. The presence of variety of heavy metals in general and the toxic ones in particular in cosmetics has raised several health concerns. It is known that toxic compounds and elements are not added, as ingredients may still be present in cosmetics because of ingredient contamination or reaction by-products. As a result, they should be kept to a minimum whenever technically feasible. Additionally, analysis of the levels of toxic heavy metal present in the marketed cosmetic products is equally important to minimize exposure to those chemicals. In this study, we determined the levels of selected toxic heavy metals Lead, Cadmium, Nickel and Chromium in five different types of cosmetic products like facial creams, face powders, lotions, hair oils, and lipsticks were collected from different cosmetic shops of Dessie town. The levels of these toxic heavy metals were determined by Flame Atomic Absorption spectroscopy after preparing the samples using standard acid digestion method. From the result Lead, Cadmium, Nickel and Chromium were detected in the ranges of 0.39-4.68 mg/kg, 1.03-4.01 mg/kg, 1.52-12.03 mg/kg and 0.96-13.36 mg/kg, respectively in all types of cosmetic samples. The one-way ANOVA Analysis between the three classes of each cosmetic samples showed that some of the samples were statistically different at ($P<0.05$) in their heavy metal concentration. The present study also showed that the cosmetics that are purchased in Dessie town are contaminated with toxic metals.

Keywords: Cosmetics, Toxicity, Heavy metals, Acid digestion.

INTRODUCTION

Cosmetic is a substance that is intended to be rubbed, poured, sprinkled or sprayed on, and introduced into human body for cleansing, promoting attractiveness, or altering the appearance and to enhance beauty (Okereke et al., 2015; Sabah et al., 2013; Siti et al., 2015). The use of cosmetics is widespread among females in particular. The psychological factors and a sense of beauty, and friendliness are the main reasons for the use of cosmetics (Tarrah et al., 2016). The use specialized forms of cosmetics is also very common in film industry in order to change physical appearances of actors (Muhammad & Stephen, 2014; Hussain et al., 2017). Women are mainly used different cosmetic products of body care as a basic daily product and they are not aware of the dangers of heavy metals and other toxic impurities that obtained in cosmetics. Even if cosmetic products have a small proportion of heavy metals; which they could not be ignored since they accumulate in the body for a long period (Aldayel et al., 2018). In recent times, certain concerns are raised regarding the presence of harmful chemicals like heavy metals in different cosmetic products (Muhammad & Stephen, 2014; Hussain et al., 2017).

Heavy metals may enter the human body via food, medication, water, absorption through the skin from cosmetics, industrial and residential settings. Contamination by these metals is series environmental and health issue as they are toxic even at low concentrations. Heavy metals which can build up in the body over time are known to cause various health problems, such as; cancer, reproductive and developmental disorders, neurological problems; cardiovascular diseases, skeletal problems, decrease in blood immune system, kidney damage and renal problems, headache, vomiting, nausea and diarrhea and organ damage which might lead to health complication or even death (Anahita et al., 2017; Mutaz et al., 2013; Okereke et al., 2015; Siti et al., 2015). In this regard, the use of underarm cosmetics has been investigated as possible cause of breast cancer (Hussain et al., 2017). Lead (Pb), when ingested in large quantities, may interfere with the synthesis of hemoglobin and calcium channels, whose

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functions are important for nerve conduction. Cadmium (Cd) may accumulate in the kidneys, with possible damage. Chronic exposure to low levels of cadmium can also cause bone fragility and consequent bone fractures. The Chromium (Cr) and Nickel (Ni) can cause allergies in skin contact (Jonathas & Thaís, 2018). The presence of Ni in many of the magic lipstick, which causes blackness and fears of the skin to sun, so the small amounts of its presence, is unsafe (Noorabdul, 2017).

Several researches have shown the presence of heavy metals in wide range of cosmetic products (Muhammad & Stephen, 2014; Hussain et al., 2017). Due to the ubiquitous nature of these elements, they can appear as impurities in various cosmetic products (Siti et al., 2015). For example, the presence of heavy metal concentrations in facial cosmetic samples have been assessed and reported to have abnormal concentrations of the metals such as Cr, Ni, Zinc (Zn) and Iron (Fe) (Muhammad & Stephen, 2014). Heavy metal elements mercury (Hg), arsenic (Ar), Cd and Pb that are able to induce toxicity even at lower levels of exposure are considered systemic toxicants (Anahita et al., 2017; Arif et al. 2015).

The cosmetic industries use different synthetic chemicals in their products. The skin of human being is permeable and the ingredients of cosmetic products can be absorbed by skin Therefore, the presence of these substances cause toxicity for human body (Agarwal et al., 2015; Niha, 2014). The aim of this study was to determine the level of toxic heavy metals Pb, Cd, Niand Cr and to compare the values obtained with international permissible limits in different cosmetic items such as facial creams, face powders, lotions, hair oils and lipsticks..

MATERIALS AND METHODS

Collection of Samples:

Samples of the most popular and common brands of cosmetics (hair oil, face powder, cream, lotion and lipsticks) were collected from various retail shops found in open markets of Dessie town. Five different types of cosmetic products (hair oil, face powder, cream, lotion and lipsticks) were selected and three classes (lower class which are less than 100 Ethiopian birr ETB, medium class about 100-200 ETB and higher class about 200-350 ETB based on the cost) were taken from each type. According to this the powder samples of High Class Powder (HCP), Medium Class Powder (MCP), Lower Class Powder (LCP), the lipstick samples of Higher Class Lipstick (HCLp), Medium Class Lipstick (MCLp), Lower Class Lipstick (LCLp), the cream samples of Higher Class Cream (HCC), Medium class Cream (MCC), Lower Class Cream (LCC), the lotion samples of Higher Class Lotion (HCLo), Medium Class Lotion (MCLo), Lower Class Lotion (LCLo), and the hair oil samples of Higher class Hair oil (HCH), Medium Class Hair Oil (MCH) and Lower Class Hair Oil (LCH). Each cosmetic type was purchased from five different shops. So, totally 15 samples were collected and labeled accordingly.

Reagents and Standards:

Analytical grade nitric acid (HNO_3, 65%) and perchloric acid ($HClO_4$, 70%) were procured from Sigma Aldrich, Germany, which were used for sample digestion. Calibration of standards for each heavy metal was prepared from the certified standard stock solution (1000 mg/kg manufactured under ISO Quality Assurance system-Perkin Elmer) in the range from 0.5 to 2 mg/kg in order to calibrate the working instrument. All the solutions were prepared in deionized water to reduce the risk in contamination of the analyzed toxic heavy metals by following the method reported previously (Hussain et al., 2017).

Sample Preparation and Digestion:

Samples of cream, lotion and hair oil (1 g) which could not be conveniently processed by dry ashing, were digested with a 80 ml of 4:1 mixture of HNO_3 (65% Sigma Aldrich) and $HClO_4$ on a hot plate in fume hood by slowly increasing the temperature till 300°C for 3 hours. Then it is allowed to cool and filtered into a standard round bottom flask (100 mL) by whatman no. 42 filter paper, and were diluted up to the mark according to the reported method. Blanks and samples were also processed and analyzed simultaneously (Kumar et al., 2012). The sample matrix of solid cosmetic samples such as face powder, lipstick (1 g) were degraded by dry ashing method using muffle furnace for 2 hours with a gradual increase in temperature up to 300°C. Furthermore, the dry ashed samples were soaked for 1 hour with a 60 ml of 4:1 mixture of HNO_3 and $HClO_4$.The solutions were again filtered into a standard round bottom flask (100 mL) by whatman no. 42 filter paper, and were diluted up to the mark.

Instrumental Sample Analysis:

This study was carried out on a Flame Atomic Absorption spectrophotometer (AAS PerkinElmer model Analyst 100) for lead (Pb), cadmium (Cd), nickel (Ni) and chromium (Cr). The readings of the instrument were rounded off suitably according to the value of standard deviation from measurements in triplicate. The major standard instrumental parameters used for the analysis of the selected heavy metals are mentioned in Table 1.

Statistical Analysis of the Result:

Statistical significance was determined by analysis of variance (ANOVA), followed by standard t-test

and p values of less than 0.05 were considered statistically significant

RESULTS

From the present study, 15 samples were analyzed for the concentration of Lead (Pb), Cadmium (Cd), Nickel (Ni) and Chromium (Cr) which are known in their toxicity for human health through their gradual accumulation. The metallic content of the three classes of each cosmetic type is described under Table 2. The result in the table showed that Pb, Cd, Ni and Cr were detected in varying concentration. As can it be seen in Table 2, all the targeted heavy metals were detected in all of analyzed cosmetic samples. According to the data obtained, the largest Pb concentration (4.68 mg/kg) was detected in higher-class face powder (HCP) whereas the smallest Pb concentration (0.39 mg/kg) was detected in lower class powder (LCP).

Similar analysis on the level of Cd in different cosmetic samples investigated shows that the largest Cd concentration (4.017 mg/kg) was detected in LCP and the smallest Cd concentration (1.03 mg/kg) was detected in medium class cream (MCC). Our study on the level of Cr also revealed the highest concentration (13.36 mg/kg) in LCP and the smallest concentration (0.96 mg/kg) in MCC. The present study on the level of Ni also showed that the significant Ni concentration (12.03 mg/kg) was detected in MCP and the smallest Ni concentration (1.937 mg/kg) was found in LCH. From the overall result Cd, Cr and Ni are found to be very large in MCP when it is compared with other cosmetic samples, which indicate that the manufacturing process is in contamination with those metals in different steps. In general the result showed that Ni > Cr > Cd > Pb in mg/kg for most of cosmetic samples.

DISCUSSION

From the result in Table 2, it can be observed that the highest concentration of the metal was detected in most of face powder sample. There have been a

Table 1: The Standard Operating Parameters of the Elements Analyzed

Element	Wavelength (nm)	Slit width (nm)	Lamp Current (mA)	Instrument Detection Limit	Method Detection Limit
Cd	228.8	0.5	4	0.002	0.01
Cr	357.9	0.2	7	0.006	0.02
Ni	232	0.2	4	0.010	0.03
Pb	217	1.0	5	0.010	0.02

Table 2: Metal concentration in the studied cosmetics samples

Sample type	Sample code	Metal concentration in mg/kg			
		Pb	Cd	Ni	Cr
Powder	HCP	4.68± 7.22	3.18±1.87	2.47±0.09	6.49±4.46
	MCP	2.38±0.57	1.99±0.22	2.61±0.41	5.99±2.51
	LCP	0.39±3.56	4.02±0.70	12.03±0.16	13.36±6.95
Lipstick	HCLp	2.53±0.39	1.81±1.03	2.47±1.30	3.05±1.47
	MCLp	1.52±0.47	1.19±0.56	3.37±2.40	2.92±1.43
	LCLp	2.55±1.22	1.48±1.04	2.81±2.19	2.67±1.73
Cream	HCC	1.01±0.30	1.22±0.71	3.05±2.49	1.71±1.13
	MCC	0.82±0.33	1.03±0.75	2.03±1.61	0.96±0.52
	LCC	0.81±0.26	1.68±1.05	2.91±1.83	2.00±1.26
Lotion	HCLo	0.81±0.59	1.12±0.55	2.65±1.58	1.90±1.25
	MCLo	0.78±0.26	1.26+0.69	1.97±1.78	1.73±1.09
	LCLo	0.47±0.70	1.25±0.74	3.22±2.22	1.60±0.98
Hair oil	HCH	1.24±0.31	1.31±0.09	1.92±1.34	2.26±1.73
	MCH	0.57±0.05	1.42±0.41	1.527±0.85	1.32±0.71
	LCH	0.74±0.24	1.36±0.16	1.937±1.26	1.93±1.68

Values are expressed as mean ± standard deviation, n=3

HCP = High Class Powder, MCP = Medium Class Powder, LCP = Lower Class Powder, HCLp = Higher Class Lipstick, MCLp = Medium Class Lipstick, LCLp = Lower Class Lipstick, HCC = Higher Class Cream, MCC = Medium class Cream, LCC = Lower Class Cream, HCLo = Higher Class Lotion, MCLo = Medium Class Lotion, LCLo = Lower Class Lotion, HCH = Higher class Hair oil, MCH = Medium Class Hair Oil and LCH = Lower Class Hair Oil.

number of recent reports discussing the presence of heavy metals in cosmetics. Pb is found in lipsticks, and hair cream in their inorganic form, and can be minimally absorbed by the skin (Jonathas & Thaís, 2018; Margit et al., 2014). When compared with previously reported data our samples were found to have less concentration of lead Pb. For example, the study, which was done in Palestine, showed that the larger amount of Pb (1.32-15.92 mg/kg) in lipstick, (2.12- 5.78 mg/kg) in foundation cream and (5.34- 9.80 mg/kg) in compact powder samples were detected (Mutaz et al., 2013). In another study, (10.9- 15.25 mg/kg) of Pb concentration was reported in different brands of lipstick sample (Ackah et al., 2015). These results generally show that most cosmetic samples are highly contaminated with lead Pb. It is known that the primary ingredients for lipstick are wax, oil, alcohol and dye (Parisa et al., 2012). Although lead is not an ingredient of the lipsticks, it might be present as an impurity, which comes from dye and wax. As it has been shown in different studies, Pb contamination in cosmetics may arise from different ways contamination in the process of manufacturing when coloring agent is added being one example (Nibras & Huda, 2014; U.S. Food and Drug Administration, 2018). Toxic compounds and elements are not added, as ingredients may still be present in cosmetics because of ingredient contamination or reaction by-products (Ekere et al., 2014; Nibras & Huda, 2014).

Previous studies have also confirmed the presence of Cd in different cosmetic products. Cadmium is commonly found in hair creams, lipsticks and skin cream (Jonathas & Thaís, 2018). In this regard 18.36 mg/kg in a face cleanser (Muhammad & Stephen, 2014), (0.01- 0.2179 mg/kg) in different powder samples (Sabah et al., 2013; Amit et al., 2010) and (0.8- 1.65 mg/kg) in different brands of lipstick samples (Ackah et al., 2015) of Cd concentrations were reported. On the other hand the study on the concentration of Cr was reported to be in the range of (9.01- 9.81 mg/kg) (Muhammad & Stephen., 2014), and (4.45-10.53 mg/kg) different powder samples (Mutaz et al., 2013). Mostly the Cr abundance in cosmetics is mainly associated with lipstick and make-up powder (Jonathas & Thaís, 2018). From the overall analysis of the present study, the highest metal concentration was detected in powder sample, which is in agreement with different reports across the different countries (Mutaz et al., 2013; Venugopal et al., 2014). Previous report also confirmed for the existence of Ni in cosmetic products (Mutaz et al., 2013). However, the level of Ni detected in the present analysis is higher than the reported values (0.032- 0.105 mg/kg) in different cosmetics samples (Adepoju-Bello et al., 2012) and (0.023-0.04 mg/kg) in lipstick (0.016-0.031 mg/kg) in face cream (0.016 - 0.022 mg/kg) as well in powder samples (Rajagopal et al., 2015). It was also reported Ni concentration in Nigeria (2.80-6.40 mg/kg) and (14.10- 39.80 mg/kg) in different lipstick and powder samples respectively in which the present study reveals smaller in comparison (Muhammad & Stephen, 2014).

It was documented that the heavy metal concentration for different brands of cosmetic samples in the ranged of (7- 30 mg/kg) for Pb, (2 - 3 mg/kg) for Ni, and (0.09 - 1.5 mg/kg) for Cd across different countries (Noorabdul, 2017). Due to the abundance of these metals in nature, everyone is exposed to small amount through cosmetics either by absorption on the skin or swallowing from lipstick. As a result, the government of Canada, Germany and FDA has implemented several measures to reduce the amount of heavy metals in cosmetic products and puts the maximum permissible limits not to exceed 10 mg/kg for Pb, 3 mg/kg for Cd and 10 mg/kg for Ni (Chan, 2012; Food and Drug Administration, 2016; U.S. Food and Drug Administration, 2018; Whitehouse, 2017).

All data obtained from Flame Atomic Absorption Spectroscopy (FAAS) analyses were calculated using (Microsoft Excel 2007) program. Analysis of variance (one-way ANOVA) was performed to identify the significant difference in metal contents with the three classes of each cosmetics sample. The one-way ANOVA analysis between the three classes of each cosmetic sample shows that Pb concentration is significantly different in hair oil sample and Cd and Ni concentrations in powder samples are statistically different at ($P \leq 0.05$). However, not all other cosmetic samples are statistically significant. That means whatever the quality of cosmetic sample is; the heavy metal concentration is nearby each other.

In conclusion, in the present study, we have investigated the concentrations of some selected heavy metals (Pb, Cd, Ni, and Cr) in different cosmetic samples marketed from Ethiopia. Our result showed that the concentration of Ni and Cr metals in the samples were above the international permissible limit in LCP. The other samples showed lower concentration when it was compared to the international permissible limit. Although the levels of some of heavy metals studied were not above the internationally permissible limits, this does not mean that it is always safe to use those cosmetic products. The continuous use of these cosmetics can increase the accumulation of heavy metals into the body by skin absorption and swallowing of lipstick leading to various diseases. Finally we recommend that use fewer cosmetics and personal care products, and less often, which can decrease the risk in exposure of toxic substances contamination of human body.

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