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The Health Risk Assessment of Some Toxic Metals in Some Commonly Demand Facial Cosmetics in Benghazi-Libya Markets During 2022

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ABSTRACT

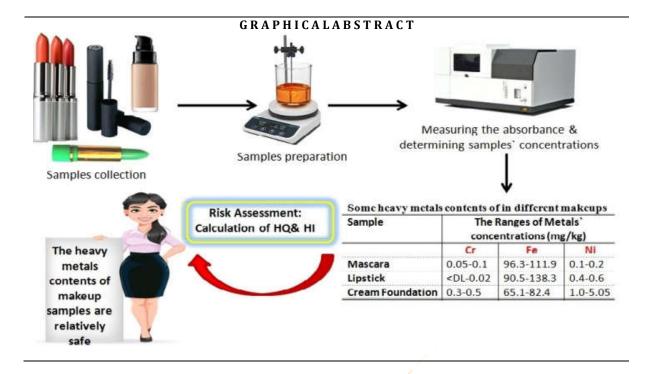
Most cosmetic products contain heavy metals. These metals are toxic and can accumulate in the body over time, causing various health effects to human health. This study aims to assess the concentrations of five heavy metals (lead, chromium, cadmium, iron and nickel) in some facial cosmetic products (foundation cream, lipstick, and mascara), collected from Benghazi cosmetic shops. Eighteen of facial cosmetic products were randomly collected from cosmetic shops. The samples were digested and analysed using Flame Atomic Absorption Spectrophotmeter. Furthermore, the non-carcinogenic and carcinogenic risk assessments were evaluated by calculating the hazard quotient (HQ) and hazard index (HI) of heavy metals in the analysed makeups. The highest mean concentrations of chromium, nickel, lead and cadmium were detected at 0.39±0.1mg/kg, 2.88±1.8mg/kg, 1.85±0.4mg/kg and 0.31±0.06mg/kg, respectively, in foundation cream samples. While the highest mean concentration of iron was detected at 117.80±22.0mg/kg in lipstick samples. The ANOVA test revealed a significant difference in the concentrations of analysed metals among the three brands of facial cosmetic products, except for chromium, nickel iron and lead metals, in mascara and lipstick products. The HQs of all metals in the selected cosmetics were <1. Also, the HI value was <1. The results of the current study demonstrated that the concentrations of the heavy metals in the cosmetic samples were within the permissible limits set by different international organizations. The risk assessment study indicated that the cosmetics were relatively safe with minimal health risks.

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Introduction

Cosmetics are defined as the products that are applied externally on the body or in the oral cavity, to cleaning, perfuming, protecting, enhancing, or altering the appearance [1]. Recently, many cosmetic products have been developed to apply to the human body for beautification [2]. These products can be classified into several categories based on their intended use and application [3]. The facial cosmetic products (makeup), or colouring cosmetic products, are a class of decorative products that used to enhance face beautifying. This class of cosmetic included lipstick and lip gloss (used to colour the lip), powder and rouge (used to colour the face, lightening and removing flaws to produce, and impression of health and vouth), eveliner and eve shadow (used to colour the eye lids), mascara (used to enhance the eye lashes), and foundation creams (applied at relatively large quantities onto the face). The foundation creams lead to the distribution of the colour pigments across the face and preventing shine [4,5]. The manufacturing of coloured cosmetic products is obtained by mixing different active ingredients, excipients, preservatives, perfumes, and mineral pigments [6]. These

pigments that used for different purposes in the cosmetic industry, are the commonly sources of the cosmetic contamination with heavy metals. Also, the raw materials of cosmetic products lead to contamination with heavy metals, which are naturally present in the environment. The cosmetic products may contaminate by using metal-coated apparatuses during cosmetic production processes [4,7].

Since the majority of cosmetics are applied to the skin, dermal exposure is expected to be the most significant route for cosmetic products. Oral exposure can also occur for cosmetics used in and around the mouth besides from hand to mouth contact after exposure to cosmetics containing heavy metal impurities [8].

Some of the common heavy metals found in cosmetics included lead, cadmium, mercury, arsenic, and chromium. These metals can pose a risk to human health and can accumulate in the body over time and cause various health effects, including skin irritation, allergies, organ damage, and even cancer [7,9]. Therefore, regulatory agencies around the world have established guidelines and limits for metals in cosmetic products to ensure consumer safety.

Health international regulation	Maximum acc	References	
	(mg/kg)		
	Pb	Cd	_
European Union (EU)	10	5	[10]
Food and Drug Administration (FDA)	20	-	[4],[7]
World Health Organization (WHO)	10	0.3	[11]
Health Canada	10	3.0	[12]

Table 1. International Standards for some heavy metals in some cosmetic products

Table 1 presents an overview of the safe levels of lead and cadmium metals in cosmetic products, along with regulatory guidelines and references [4,7,10-12]. Table 1 shows that the safe levels of both lead and cadmium metals in cosmetic products were varied depending on the metal, the regulation agencies or country [4,7,10-12]. Furthermore, for skin protection, the FDA that nickel and suggested chromium concentrations should be less than 1.0 mg/kg in cosmetic products [7,11].

In recent years, different studies have investigated the levels of toxic heavy metals in facial cosmetics, in different countries around the world. Even more, several studies have evaluated the non-cancer and cancer risk assessments of heavy metals in the analysed cosmetic products [7,13-16]. As the using of cosmetic products is increasing rapidly in Benghazi-Libya, there is limited research available on the topic of heavy metals exposure from facial cosmetic products. In fact, only one study conducted by Rahil *et al.* to detect the levels of heavy metals in some facial cosmetic products collected from cosmetic shops

in Benghazi city. This study recognizes whether the metals' concentrations were within the ranges of the permission limits recommended by the World Health Organization (WHO) for toxic metals in cosmetics [17]. However, Rahil *et al.* work has not evaluated the health risk assessment of heavy metals in analysed cosmetics. Therefore, the aim of the present study is to analysis five toxic metals in the highly seller facial cosmetic products in cosmetic shops of Benghazi, and calculated the possible health risk effects of the analysed metals on human health.

Experimental

Facial cosmetic samples collection

In the current investigation, 18 face cosmetic products were randomly selected and sold from different cosmetic shops within the city of Benghazi, comprising 6 lipsticks, 6 mascaras, and 6 foundation creams. The samples were classified and coded as recorded in Table 2 with abbreviation "M" for Mascara, "L" for Lipstick and "F" for foundation cream samples.

Cosmetic type Code number		Color	Manufacture country	
Mascara	M1	Ultra-black	China	
	M2	Black	Turkey	
	M3	Black	Italy	
Lipstick	L1	Red	-	
	L2	Dark brown	-	
	L3	Green- magic lipstick*	China	
Foundation	F1	Natural	Poland	
Cream	F2	Natural	Italy	
	F3	Soft cream	France	

Table 2. List of facial cosmetic samples collected from cosmetic shops in Benghazi	
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(-) Not available, the expiration dates for mascara and cream foundation listed on the products were 12 and 6 months after product opening, respectively.

(*) This lipstick contains Red 27, which is a synthetic colorant azo-dye. This dye imparts vibrant shades pink, depending on the pH and temperature of consumer's lips.

Preparation of facial cosmetic samples for metal analysis

The same brands of each makeup samples were mixed for homogeneity. These samples were digested using concentrated acids mixture, nitric acid, sulphuric acid and perchloric acid (in ratio 1:1:1), following the procedure reported Ayenimo 2010 [18]. One gram of each sample was weighed into 50 mL beaker and 10 mL of a concentrated acids mixture were added. The mixture was kept overnight at room temperature. Then, the sample was heated at 60 °C for 15 minutes. The temperature was gradually increased to 130 °C, and the mixture was heated for 1 hour. After the digestion process, the solutions were left to cool, then transferred into a 25 mL volumetric flask and diluted with deionized water. The sample solutions were filtered using filter papers (Whatmman 41). The metals in the digested solutions were analysed using double beam GBC model 932 Plus Flame Atomic Absorption Spectrometer. This instrument consists of a four-lamp turret, a deuterium lamp for background correction, an optical system incorporating a chopper, mirrors, lenses, monochromator, a 10cm burner head and air-acetylene flame and photomultiplier detector. The wavelengths were selectable between 185 to 900 nm via an 1800 line/mm grating. The absorbance measurements were performed at room temperature, using a computer controlled system with GBC AA Avanta Software, version 1.33. The operating conditions in the spectrometer were adjusted according to the standard guidelines of the manufacture. The quantitative estimation of each analysed metal based on using the corresponding calibration curve of each analysed metal [18].

Statistical analysis

All the analytical data of analysed metals were performed in duplicate, and the results were expressed as mean (mg/kg) ±standard deviation (mean ±SD) for each sample. The results of each metal were expressed as ranges (min-max). The comparisons between the facial cosmetic products were performed by the One-Dimensional Variance Analysis (One-way ANOVA) test, followed by Least Significant Difference (LSD) test. All the statistical analysis was carried out using statistical package for social science (SPSS version 19) Program, adopting the significance level of 5% (P < 0.05).

Health risk assessment method

The human risk models including noncarcinogenic and carcinogenic ones established by the United States-Environmental Protection Agency (US-EPA) were adopted. These models and their threshold values were employed to assess the potential human health risks posed by the analysed metals in the selected facial cosmetic samples [19,20].

Chronic daily intake

In this study, the calculations of the Chronic Daily Intake (CDI) of the toxic heavy metals via dermal contact with makeup particles were carried out using Equation (1) [21,22].

$$CDI_{dermal} = \frac{CS \times SA \times AF \times ABS \times EF \times ED}{BW \times AT} \times 10^{-6}$$
 (1)

The detailed explanation for the parameters in equation (1) was listed in Table 3.

Exposure Factor	Value-Unit		
Concentration of metal in makeup sample (CS)	mg/kg		
Exposed skin area (SA)	5700 cm ²		
Adherence Factor (AF)	0.07 mg cm ⁻²		
Dermal Absorption Fraction (ABS)	0.001		
Exposure Frequency (EF)	350 days/year		
Exposure Duration (ED)	30 year		
Average time for non-carcinogens (AT)	=365×ED		
Body Weight (BW)	70 kg		

Hazard quotient and hazard index

The Hazard Quotient (HQ) is calculated as the ratio of exposure to toxic metal via dermal contact (CDI) to the chronic dermal Reference Dose (RFD) of each toxic metal (in mg/kg/day), as described in Equation (2) [20].

$$HQ_{HM} = \frac{CDI_{dermal}}{RFD_{dermal}}$$
(2)

The RFD values were 10, 3, 3, 20, and 360 μ g/kg/day for cadmium, lead, chromium, nickel, and iron, respectively [22] if the value of HQ < 1, the exposed population is unlikely to experience obvious adverse effects. If HQ > 1, there is a potential health risk, and related interventions and protective measurements are needed to be taken [21]. On the other hand, the Hazard index (HI) is the sum of the hazard quotients for all heavy metals, as explained by Equation (3).

$$\begin{split} \mathrm{HI} &= \sum_{i=1}^{n} \mathrm{HQ}_{i} = \mathrm{HQ}_{\mathrm{Cr}} + \mathrm{HQ}_{\mathrm{Fe}} + \mathrm{HQ}_{\mathrm{Ni}} + \mathrm{HQ}_{\mathrm{Pb}} + \\ \mathrm{HQ}_{\mathrm{Cd}} \eqno(3) \end{split}$$

When the HI value as <1, indicated that the exposed population has not experienced any evident adverse effects, but if the HI \ge 1 it is dangerous for the makeup consumers [19,20].

Results and Discussion

Using the cosmetic products for a long time may cause many health problems due to the presence of heavy metals, which can entered in the body through dermal absorption. Even though, using metals as ingredients in cosmetics is forbidden in many developed countries. However, these metallic impurities exist naturally in the environment. Therefore, they cannot be avoided, even under good manufacturing practices [7,22]. In this study, the concentrations of five heavy metals were analysed in three different facial cosmetic products commonly seller in Benghazi's cosmetic shops. The results of analysis of toxic heavy metals, including chromium, iron, nickel, lead, and cadmium in the collected facial cosmetic samples were summarized in Table 4.

Sample	Concentration of metals (mg/kg)*					
	Cr	Fe	Ni	Pb	Cd	
M1	0.045 ± 0.002	96.31±1.5	0.16 ±0.003	0.80±0.02	0.091±0.004	
M2	0.10±0.002	111.93±0.11	0.22 ±0.004	0.11 ±0.002	<dl< td=""></dl<>	
M3	0.054±0.002	100.05±0.07	0.11 ± 0.001	1.068 ±0.045	<dl< td=""></dl<>	
Mean ± SD	0.066 ±0.03	102.80 ±7.3	0.16 ±0.05	0.66 ±0.44	0.030 ±0.05	
(n = 6)						
Range	0.045-0.1 🧹	96.31-111.93	0.11-0.22	0.11-1.068	<dl-0.091< td=""></dl-0.091<>	
L1	<dl< td=""><td>124.47 ±0.2</td><td>0.58 ±0.01</td><td>0.066 ±0.005</td><td>0.12 ± 0.002</td></dl<>	124.47 ±0.2	0.58 ±0.01	0.066 ±0.005	0.12 ± 0.002	
L2	<dl< td=""><td>90.51 ±2.0</td><td>0.50 ±0.001</td><td>0.21 ± 0.001</td><td>0.13 ±0.005</td></dl<>	90.51 ±2.0	0.50 ±0.001	0.21 ± 0.001	0.13 ±0.005	
L3	0.020 ±0.003	138.27±1.3	0.42 ±0.005	0.098 ±0.003	0.20 ±0.003	
Mean ± SD	0.0067 ±0.01	117.80±22.0	0.45 ±0.07	0.12 ± 0.07	0.15 ± 0.04	
(n = 6)						
Range	<dl-0.020< td=""><td>90.51-138.27</td><td>0.42-0.58</td><td>0.066-0.21</td><td>0.12-0.20</td></dl-0.020<>	90.51-138.27	0.42-0.58	0.066-0.21	0.12-0.20	
F1	0.34 ± 0.004	74.76 ±1.3	1.020 ± 0.04	1.94 ±0.03	0.30 ±0.005	
F2	0.52 ± 0.008	82.41 ±1.2	2.56 ±0.3	1.50 ± 0.7	0.25 ±0.004	
F3	0.30 ± 0.008	65.13 ±1.2	5.051 ±0.04	2.11 ±0.004	0.38 ±0.005	
Mean ± SD	0.39 ± 0.10	74.10 ±7.8	2.88 ±1.8	1.85 ± 0.4	0.31 ± 0.06	
(n= 6)						
Range	0.30-0.52	65.13-82.41	1.020-5.051	1.50-2.11	0.25-0.38	

Table 4 . The contents of some heavy metals in different makeup samples collected from cosmetic shops in
Benghazi City

*Each value is the average of two separated determinations. < DL= Below Detection Limit. The DLs for Cd, Fe, and Pb are 0.5, 3, and 10 ppb, respectively. The DL for both Cr and Ni is 2ppb.

Regarding to our study, the mean concentration of the analysed metals in the selected facial cosmetic products were found in the order of cadmium <chromium <nickel <lead <iron, chromium <lead <cadmium <nickel <iron and cadmium< chromium< lead<nickel <iron in mascara, lipstick and foundation cream samples, respectively. In all mascara samples, the concentrations of chromium, iron, nickel, and significant and the lead were mean concentrations of these metals ranged between 0.045-0.10 mg/kg, 96.31-111.93 mg/kg, 0.11-0.22 mg/kg, and 0.11-1.068 mg/kg, respectively. Whereas, cadmium was only detected in M1 sample at concentration 0.091 ±0.004 mg/kg. In all lipstick samples lead, chromium, nickel, iron, and cadmium were also detected. The total concentration of lead and cadmium in the lipstick samples ranged from 0.066 to 0.21 mg/kg, and from 0.12 to 0.20 mg/kg, respectively, while the concentrations of chromium, nickel, and iron ranged at <DL-0.020 mg/kg, 0.42-0.58 mg/kg, and 90.51-138.27 mg/kg, respectively. The results of our study revealed that the analysed metals were detected in all foundation cream samples. The highest concentration of lead and cadmium were detected at 2.11±0.004 mg/kg and 0.38±0.005 mg/kg in sample F3, respectively. Furthermore, the maximum concentrations of chromium, and iron were detected at 0.52±0.008 mg/kg and 82.41±1.2 mg/kg in F2 sample, respectively, while the highest concentration of nickel was detected in ample F3 at 5.051±0.04 mg/kg.

Among the heavy metals concentrations data presented in Table 4, it reveals that chromium was detected in all collected makeup samples except two lipstick samples, where chromium levels were below the detection limit of employed analysis method. The maximum concentration of chromium was quantified in foundation cream. Chromium metal has the ability to accumulate in the liver and kidneys, cause skin rashes and weakness in the efficiency of the immune system [12,23].

Furthermore, our study revealed that nickel metal was detected in all makeup samples. Nickel metal is a basic constituent of diet, but its elevated concentration resulted in asthma, vomiting, skin allergies, conjunctivitis, and lung fibrosis [24]. The mean concentration of nickel in mascara and lipstick samples was detected at 0.16±0.05 mg/kg and 0.45±0.07 mg/kg, respectively. In fact there is no significant difference in the concentration of nickel metal in all brands of mascara and lipsticks (P=0.589). Even more, the concentrations of nickel metal in mascara and lipstick products were lower than FDA regulation. While, the highest nickel mean concentration (2.88±1.8 mg/kg) was detected in foundation creams. The nickel concentrations in foundation creams were higher than 1mg/kg [4,7].

Generally, iron is considered as an important mineral nevertheless its exceeding level may cause serious health issues [7]. In all samples of makeup, variation significant levels of iron were detected, with the highest concentration in lipstick, followed by mascara, and then foundation cream samples. The ANOVA show a significant difference (P=0.00) between the levels of iron in foundation cream and other makeup products. However, the mean concentration of iron in our lipstick samples were relatively higher than mean concentration of iron in lipstick samples collected from Benghazi markets, previously published by Rahil et al. [17]. In fact, there is no internationally accepted upper limit for iron in cosmetic products [17]. However, excess iron accumulates over time in human body organs such as the brain and liver, causing liver problems, heart failure, colorectal cancer, and finally cellular death [16,23,25].

In this study, the lead concentration was found in the all samples, the highest lead mean concentration was detected in foundation cream samples (1.85±0.4 mg/kg), while the lowest concentration (0.12±0.07 mg/kg) was detected in lipstick samples. Lead is a proven neurotoxin associated with learning language and behavioural problems [18,23]. It also causes adverse effects on many organs and systems including the central nervous system, the kidneys, and the hematopoietic system [12]. The results of this study showed that all the samples contain lead metal under the permissible limits of different international regulations [10-12]. However, lead metal can enter through the pores in the skin and accumulate in the human body [26]. The toxic cadmium metal was detected in

some samples. The highest mean concentration of cadmium (0.31±0.06 mg/kg) was detected in foundation creams, where cadmium consequently absorbed into the body through dermal contact [5,26]. The levels of cadmium in some foundation creams were similar to the respective WHO maximum allowable limit [11]. In fact, this metal is classified as a human carcinogen by the National Institute for Occupational Safety and Health, and can cause irritant dermatitis [12,26].

Health risk assessment of the toxic metals in facial cosmetic samples

In this study, the CDI, HQ, and HI terms were used to evaluate the potential health risks associated with dermal exposure to heavy metals. The CDI of the analysed metals were shown in Table 5. These values ranged at $8.86 \times 10^{-7} - 1.02 \times 10^{-4}$ mg/day for chromium, $1.71 \times 10^{-4} - 0.18$ mg/day for iron, $6.62 \times 10^{-6} - 1.85 \times 10^{-3}$ mg/day for nickel, $4.26 \times 10^{-6} - 1.03 \times 10^{-3}$ mg/day for lead, and $7.11 \times 10^{-7} - 2.35 \times 10^{-4}$ mg/day for cadmium. In both mascara and cream foundation samples, the mean values of CDI of the toxic metals were decreased in order: iron> nickel>lead>chromium> cadmium. While in lipstick samples the order of CDI values of toxic metals decreased in order: iron> nickel> cadmium> lead> chromium. The CDI values of heavy metals in all cosmetics were lower than maximum tolerable daily intake of heavy metals over a lifetime without significant risk to human health [27].

On the other hand, the non-carcinogenic risk from the individual toxic metal in cosmetic samples, expressed as HQ and the carcinogenic risk (expressed as HI) of the analysed heavy metals in the collected makeup samples were shown in Table 6. The HQ_{dermal} of all analysed metals were less than unity, which indicating that consumers in Benghazi would not experience any significant health risk via dermal adsorption of the studied makeup brands. Furthermore, the data in Table 6 revealed that the HI values were recorded at 2.1×10^{-4} , 2.0×10^{-2} , and 5.0×10^{-2} in foundation cream, mascara and lipstick, respectively.

	Chronic Daily Intake (CDI)			
		(mg/da	y)	
Heavy metal	Facial Cosmetic Products			
	Mascara	Lipstick	Foundation cream	
Cr	1.02×10 ⁻⁴	1.04×10 ⁻⁵	8.86×10 ⁻⁷	
Fe	0.16	0.18	1.71×10 ⁻⁴	
Ni	∕1.85×10 ⁻³	7.0×10 ⁻⁴	6.62×10-6	
Pb	۱.03×10-3	1.91×10 ⁻⁴	4.26×10-6	
Cd	4.70×10 ⁻⁵	2.35×10-4	7.11×10 ⁻⁷	

Table 5. The chronic daily intake of heavy metals in the selected facial cosmetic samples

 Table 6. The Dermal Hazard Quotient (HQ) and Hazard Index (HI) of heavy metals detected in collected facial

 cosmetic samples

Cosmetic product	HQ _{Cr}	HQ _{Fe}	HQ _{Ni}	HQ _{Pb}	HQ _{Cd}	HI
Mascara	6.82×10 ⁻³	1.14×10 ⁻³	3.43×10 ⁻⁴	2.44×10 ⁻³	9.40×10 ⁻³	2.0×10 ⁻²
Lipstick	6.92×10 ⁻⁴	1.31×10-3	1/30×10-4	4.56×10-4	0.047	5.0×10 ⁻²
Foundation cream	5.91×10 ⁻⁵	1.22×10 ⁻⁶	1.23×10 ⁻⁶	4.26×10 ⁻⁶	1.42×10^{-4}	2.1×10 ⁻⁴

The HI values for the carcinogenic effects of the analysed toxic metals indicated that the consumers of the selected facial cosmetics are safe. However, the prolong using of cosmetics may allow the accumulation of toxic elements in the human body either through adsorption or absorption through the skin and finally entering the blood stream [28]. Long-term studies found a correlation between the elevated levels of toxic elements and kidney failure [29], negative impacts on retinal epithelium pigments [28], cardiovascular and neurologic disorders [30], and hepatotoxicity [31].

Conclusion

Since the beginning of civilization, the beauty products considered as a part of routine body care. Heavy metals are often present in cosmetics as impurities or as intentional ingredients. The prolonged and intensive use of these cosmetic products may cause the heavy metals to slowly release and harm the users. It is important for consumers to be aware of the metallic ingredients in the cosmetics they use and to follow safety guidelines to minimize any potential health risks. According to our results of the elemental analysis, all the facial cosmetic samples included lead, chromium, nickel, iron, and cadmium metals. The concentrations of these toxic heavy metals were lower than the permissible limits of international organizations. In addition, no metals were found to be considered as potential health hazard for human. This study recommends the continuous monitoring of toxic metals in other items of cosmetics and establishing strict rules for internationally accepted limits for the presence of these metals in cosmetic and body care products. This study also recommends educating the general public, particular the women, about the presence of toxic metals and the potential toxic effects of accumulated metals and other polluting substances in cosmetics products.

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Declarations

Conflict of interest: The authors have no relevant financial or non-financial interests to disclose. Ethical approval: Not applicable. Consent to participate: Not applicable. Consent for publication: Not applicable

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