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Determination of Some Heavy Metals in Some Cosmetic Products (Foundation, Blusher, and Face Powder) By Atomic Absorption Spectrometer

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Abstract:

The concentrations of Lead (Pb), Cadmium (Cd), Chromium (Cr), Manganese (Mn) and Zinc (Zn) in three brands of cosmetics; Five type from each foundation cream, blush and face powder, all samples were collected in during April 2023, from Benghazi city markets in the east of Libya. After wet digestion, the samples were analyzed using atomic absorption spectrophotometer. The mean concentrations observed in the cosmetic samples of foundation cream ranged between 0.00 to 2.10 mg/kg of Pb; 0.13 to 7.56 mg/kg of Cd; 0.17 to 2.69 mg/kg of Cr; 0.00 to 12.89mg/kg of Mn and 3.53 to 11.25 mg/kg of Zn.

While the mean concentrations observed in the cosmetic samples of blusher ranged between 0.00 to 10.98 mg/kg Pb; 1.95 to 7.48 mg/kg Cd; 0.00 to 8.89 mg/kg Cr; 0.26 to 0.65mg/kg Mn and 1.14 to 18.59mg/kg Zn. and the mean concentrations observed in the cosmetic samples of face powder ranged between 1.76 to 5.92mg/kg Pb; 0.00 to 3.24 mg/kg Cd; 0.00 to 10.89 mg/kg Cr; 0.39 to 3.84mg/kg Mn and 0.17 to 6.51mg/kg Zn. all study samples were subjected to microorganism analysis and all results were negative, meaning they were free of any bacterial contamination. However, chemical analysis showed that, the results obtained revealed that Pb, Cd and Mn in most samples of study were higher than WHO permissible limits (World Health Organization). However, it would be preterm to jump into conclusion to decide the fates of the analyzed 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 Libya 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, Foundation cream, Toxic heavy metals, AAS.

تحديد بعض المعادن الثقيلة في بعض مستحضرات التجميل (كريم الأساس، أحمر الخدود، وبودرة الوجه) باستخدام مطياف الامتصاص الذري

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الملخص

في هذه الدراسة تم تقدير تركيز بعض المعادن الثقيلة مثل الرصاص والكادميوم والكروم والزنك، من مساحيق التجميل (كريم الأساس - مسحوق احمر الخدود – بودرة الوجه) من كل نوع تم اختيار 5 ماركات مختلفة من أسواق مدينة بنغازي في شهر ابريل سنة 2023 في الشرق الليبي. حيث اخذت العينات بشكل عشوائي وتم تحليلها بعد التهضيم المناسب لكل نوع من أنواع عينات مساحيق التجميل وقياس تركيز المعادن المبينة أعلاه باستخدام جهاز المطياف الضوئي المتوفر في جامعة بنغازي بقسم الكيمياء.

أخضعت كل العينات الي التحليل البيولوجيا و الكيميائي فكانت كل العينات خاليه من أي تلوث بيولوجي وكانت معظم نتائج الدراسة المتحصل عليها بعد تقدير المعادن الثقيلة باستخدام جهاز المطياف الضوئي تدل علي وجود كميات عالية من المعادن الثقيلة بنسب متفاوتة , وكانت أعلي من الحدود المسموح بها من قبل منظمة الصحة العالمية , فكانت معظم النتائج المتحصل عليها تدل علي وجود كميات عالية من المعادن الثقيلة بنسب متفاوتة، وكانت أعلي من الحدود المسموح بها من قبل منظمة الصحة العالمية ، وهذا الامر خطير لمستخدمي مستحضرات التجميل وذلك لتعرضهم للأثار الضارة، عند الافراط في استهلاك مستحضرات التجميل وتراكم المعادن الثقيلة في الجسم.

الكلمات المفتاحية: مستحضرات التجميل، كريم الأساس، المعادن الثقيلة، جهاز المطياف الضوئي.

Introduction

Cosmetics are anything that can be applied to the human mouth, teeth, and other external areas of the body, and any preparation or substance designed to be applied on these areas is defined as Cosmetics. Cosmetics are used primarily for cleaning, perfuming, protection, enhancing appearance, removing body odor, and maintaining surface cleanliness [1]. Lead, cadmium, nickel, manganese, arsenic and mercury, chromium, iron, copper, and cobalt are among the thousands of hazardous chemical substances that can be found in cosmetic products [2-4].

industrialization is on the rise worldwide, leading to greater exposure of humans to heavy metals, making them more prone to exposure than ever before in modern history. Heavy metals are present in industrial sludge, which are responsible for contaminating industrial waste by being released near agricultural fields or mixed with soil. These metals are then taken by cosmetics and then transported to human consumption. The rising risk of heavy metals contamination has led to the need for testing cosmetics before consuming it to ensure safety.

A number of literatures, including well-known studies, have provided ample evidence in over two decades regarding the presence of lead and cadmium in cosmetics, being a particularly well-known case study. These studies have identified lead and cadmium in cosmetics as potential sources of toxic poisoning in neonates due to their ability to resorb these metals. Several studies have reported cases of lead poisoning or impregnation due to the use of cosmetic, a popular cosmetic product [5].

Because of the negative impact of metals on human health, the presence of these metals in cosmetic products is restricted by various global health regulations and health legislation in several countries, including Germany, Canada, Jordan, and EU nations. The regulations and limits in question aim to guarantee a high degree of safety for consumers. Heavy metals lead to heightened health hazard levels due to the toxic effects they can have on humans. it is necessary to monitor commercially available cosmetics regarding the concentrations of metals, in order to recognize whether the concentrations are within the safe values ranges.

Human health is therefore of great significance. To evaluate cosmetic samples, the metal is scrutinized using atomic absorption spectrometry (AAS), to analyses individual components of the sample, such as its composition, molecular structure, and analytical chemistry. Before weighing the heavy metals, a digestion process must be carried out on cosmetic samples, to convert the components of the matrix into basic chemical forms, before the quantification. Various techniques, such as wet-digestion and dry-ashing digestion, have been suggested to prepare cosmetic samples for elemental analysis [6- 9].

The existence of toxic metals in colored cosmetics has been extensively covered in reports from across the Arab World, with indications of exposure to these substances. There has been no investigation into the heavy metal contamination in samples taken from cosmetic product shops in Benghazi (Face foundation, Blusher and Face powder). Despite efforts, no attempts have been made to investigate the presence of heavy metals such as lead, cadmium, iron, copper, chromium, and zinc [10-15].

Microbiology of Cosmetics Study:

Microorganisms' contamination depends on the product composition. Content of preservatives, manufacturing hygiene. Packaging, transport and storage.

A lot of microorganisms can enter to the product via hand and mouth [16]. Raw materials can contribute to a significant level of microbial contamination to the finished product Testing of raw materials before use. Most of the cosmetic products with the high-water content were at risk of being contaminated by microorganisms and pose a health risk to consumer [17].

All culture media (nutrient broth medium, sabouraud dextrose broth with chloramphenicol, mannitol salt agar medium, nutrient agar medium, MacConkey agar medium, sabouraud dextrose agar with chloramphenicol) were purchased from Oxoid, HiMedia and Bacto.

Methods

Collection of samples

Fifteen samples were taken from Benghazi city markets in the east of Libya in April 2023, five types of foundation cream, blusher, and face powder were found in different types available at different prices.

Design and Setting
Analytical reagent-grade chemicals (65% of HNO_3 and 30% of H_2O_2) Ultrapure water was used for preparation of working reagents and for sample dilution. The glassware was cleaned and immersed in 6% nitric acid for 24 h. Teflon beakers were treated with 6% nitric acid and washed with ultrapure water. Using a hot block digester (Grant QBT2 Digital Block Heater, England), the **Blusher - face powder** samples were broken down using 5.0 ml of nitric acid and 2.5 ml of hydrogen peroxide. For 15 minutes, the sample was heated to 60°C. After that, the heat was raised to 130°C and allowed to digest for one hour [14,15]. The foundation samples were thoroughly blended after being crushed in an agate mortar. Two milliliters of nitric acid, two milliliters of sulfuric acid, and one milliliter of perchloric acid were put to a test tube containing approximately 0.25 grams of each sample [1]. Following digestion, sample solutions were cooled before being transferred into a 25 ml volumetric flask. Rinsing with deionized water multiple times eliminated the sample that was still in the tube. To bring the solution up to par, the washing water was combined with the prior sample in the flask. Whatman No. 41 filter paper was then used to filter the sample solution. FAAS was used to measure each sample solution's absorbance. (GBC model 932 Plus FAAS with GBC Avanta Software, version 1.33, GBC Scinetific Eqipment Ltd., Braeside, Victoria, Australia), Table 1. Shown the condition measurements of the studied elements.
The absorbance versus concentration curves of the standard solutions were used to calculate the elemental concentrations in the sample solutions. The same conditions were used to prepare blank solutions. [13].

Table 1. Working conditions for AAS measurements

Operation Parameter	Elements				
	pb	cd	Mn	Cr	Zn
Wavelength (nm)	217.00	228.00	279.48	357.90	213.90
Bandpass (slit width) (nm)	0.5	0.5	0.2	0.2	0.7
Lamp current (mA)	5	4	4	7	8
Height of the burner (mm)	12	12	12	12	12
Air flow rate (L/min)	4.5-4	4.5-4	4.5-4	4.5-5.5	4.5-4
Optimum Working Range (µg/mL)	0.1-2.5	0.04-1.8	1.0-5.0	0.01-1.0	0.4-1.5
Sensitivity (µg/L)	120	12	40	25	11
Detection limit (µg/kg)	0.6	1.0	0.37	2.0	1.4
Correlation coefficient (r)	0.9997	0.9991	0.9988	0.9907	0.9991

Media Used for Growth of Bacteria
MacConkey and Blood agar were used for growth of bacteria provided from OXOIDE (Germany), and Sabauroud`s Dextrose agar from HIM MEDIA LABORATORIS PVT. Ltd (India) was used to grow moulds. All these media were prepared under aseptic conditions, according to the manufacture's specifications. Ethanol, from MERCK (Germany) was diluted to 70% (v/v) and used for the disinfection of the sample package.

Microbiology's method
The collected cosmetic samples were aseptically transferred to microbiological lab; two weights of 1 gram for each sample were measured. The first 1 gram were aseptically placed into 50ml of nutrient broth containing duram bottle and incubated at 37°C for 24hours. Other 1 gram were placed into 50ml of sabaroud dextrose broth containing duram bottle and incubated at 25◦C for 72 hours in order to detect bacterial and fungal contamination respectively [18, 19]. After incubation, cultures in nutrient broth were streaked onto nutrient agar, macConkey agarand mannitol salt agar while the cultures from sabouraud dextrose broth were streaked onto sabouraud dextrose agar.

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% ($P < 0.05$).
The obtained data was also tested by Kruskal-Wallis Test.

Results:
Contaminating cosmetic products for an extended period of time can lead to health issues as heavy metals can be ingested through the gut, causing the individual to be exposed to toxic metals in the product, which can then be

absorbed by the body. In numerous developed nations, the production of cosmetic metals is prohibited in many developed nations. Even though they have metallic nature, these metallic impurities are still present in nature. Although good manufacturing practices [1,20] are prevalent, they cannot be completely wiped out. This study investigates techniques for identifying potential cancer risk factors in individuals with high occurrences of the disease.

Table 2. shows the studied cosmetics samples and some of their information, in this study, heavy metals were estimated using FAAS in the three different brands of cosmetic s. Table.3, listed some of the International Standards for some heavy metals in cosmetic products.

Table 2. List of cosmetics, their codes, and container label disclosures of the collected samples

Cosmetic product	Sample code	Color of product	Country of manufacture	Name of Product
Fundation Cream	A1	Light vanilla	Italy	Mac
	A2	Veela beauty	Polanda	MaxFacter
	A3	Matte	China	Boujois
	A4	Dark amber	Italy	FinalTough
	A5	Sun cream	China	Dermalys
Blusher	B1	Light pink	Ireland	Seven cools
	B2	Velvety	Italy	Flormar
	B3	Dark pink	Italy	Gosh
	B4	40 pinks	Polanda	Maybelline
	B5	Red (2)-glow	Ireland	BBrose
Face Powder	C1	Max	China	Danni
	C2	Light bronze	Italy	Bourjois
	C3	Natural Beige	China	Sephora
	C4	Dark amber	China	Flomar
	C5	Amber	China	Hudabutay

Concentrations of five heavy metals were also found in three different brands of cosmetic products that were sold in cosmetic shops in Benghazi using flame atomic absorption spectrophotometer (FAAS).
Comprehensive analysis of collected facial cosmetic samples revealed the presence of toxic heavy metals, including chromium, zinc, manganese, lead, and cadmium, which were significantly associated with levels of toxicity, as shown in Table 4.

Table 3. International Standards for some heavy metals in some cosmetic products

Health international regulation	Maximum acceptable limits (mg/kg)		Reference
	Pb	Cd	
European Union (EU)	10	5	[17,20]
Food and Drug Administration (FDA)	20	-	[21]
World Health Organization (WHO)	10	0.3	[22-23]
Health Canada	10	3.0	[24]

Significant levels of Cr have been found in all cosmetic samples in rang 0.11±0.01mg/kg in foundation cream, in 0.35±0.13 mg/kg in blusher samples, and 0.53±0.19 mg/kg in face powder. This low concentration of chromium was detected. Manganese metal was detected in all cosmetic samples, in rang 0.70±0.11 mg/kg for foundation cream, .27±0.01 mg/kg for busher samples and 0.29±0.03 mg/kgfor face powder samples. Zinc metal was detected in rang 0.92±0.11 mg/kg for foundation cream samples, 0.71±0.01 0mg/kg for blusher samples and 5.74±0.38 mg/kg for face powder samples. Although some metals such as chromium, Manganese, iron, and zinc, in trace amounts, play important biochemical roles in many organisms, the toxic effects are observed at high concentrations. All those metals can lead to damaged or reduced central nervous system functions and damage to blood composition, lungs, kidney, liver, and other vital organs. Long-term exposure may result in slowly progressive physical, muscular, and neurological degenerative processes that mimic Alzheimer's disease, Parkinson's disease, muscular dystrophy, and multiple sclerosis [25].

Table 4. Concentration of pd, Cd, Cr, Zn and Mn in cosmetic samples (mg/Kg)

Cosmetic product	Sample code	Pb±SD	Cd±SD	Cr±SD	Zn±SD	Mn±SD
Fundation Cream	A1	1.34±0.21	0.01±0.05	ND	2.62±0.00	0.21±0.21
	A2	0.55±0.02	11.33±0.01	0.10±0.01	0.20±0.01	1.10±0.02
	A3	ND	1.11±0.21	0.30±0.03	0.30±0.02	0.45±0.00
	A4	2.57±0.31	0.94±0.01	0.04±0.23	0.64±0.23	0.80±0.11
	A5	0.00±0.00	0.42±0.02	0.10±0.01	0.82±0.31	0. 92±0.23
	Mean±SD (*n*=3)	0.89±0.11	2.68±0.06	0.11±0.01	0.92±0.11	0.70±0.11
Blusher	B1	0.25±0.01	0.00±0.00	1.11±0.41	1.21±0.20	0.02±0.01
	B2	0.66±0.42	0.00±0.00	0.11±0.02	1 .90±0.01	1.21±0.01
	B3	1.01±0.00	8.21±0.11	0.01±0.01	0.33±0.01	ND
	B4	ND	0.30 ±0.01	0.44±0.20	1.20±0.21	0.10±0.01
	B5	0.53±0.21	2.41±0.12	ND	0.11±0.01	0.01±0.00
	Mean±SD (*n*=3)	0.49±0.13	2.18±0.05	0.35±0.13	0.71±0.01	0.27±0.01
Face Powder	C1	0.20±0.02	ND	0.45±0.31	16.16±0.41	0.20±0.04
	C2	0.60±0.03	0.23±0.01	0.52±0.21	7.40±0.53	0.22±0.03
	C3	0.30±0.10	0.12±0.01	0.00±0.0	2.77±0.34	0.60±0.02
	C4	0.20±0.11	ND	1.10±0.31	0.83±0.41	0.10±0.00
	C5	0.20±0.10	0.01±0.00	0.23±0.11	1.55±0. 20	0.34±0.04
	Mean±SD (*n*=3)	0.30±0.05	0.07±0.01	0.53±0.19	5.74±0.38	0.29±0.03

[a]Each value is the average of two separated determinations, ND: Not detected, SD: Not detected

Figure 1a. show us the concentration of lead (Pb) and cadmium (Cd) of the studied cosmetics samples by mg/kg The results showed that the concentration of Cd was high in most of the samples studied, as it was A2 has the highest concentration of Cd then B3 and B5.

The P value for the analysis results corresponding to 0.599 and 0.029, respectively, Table 4. for the toxic metals present in cosmetic samples. There were no major differences in the categories of lead-based cosmetic products compared to cadmium, but cosmetic products showed no significant differences, as suggested by these values, with minimal differences for lead (both listed as cadmium and trace amounts were found for cosmetic purposes).

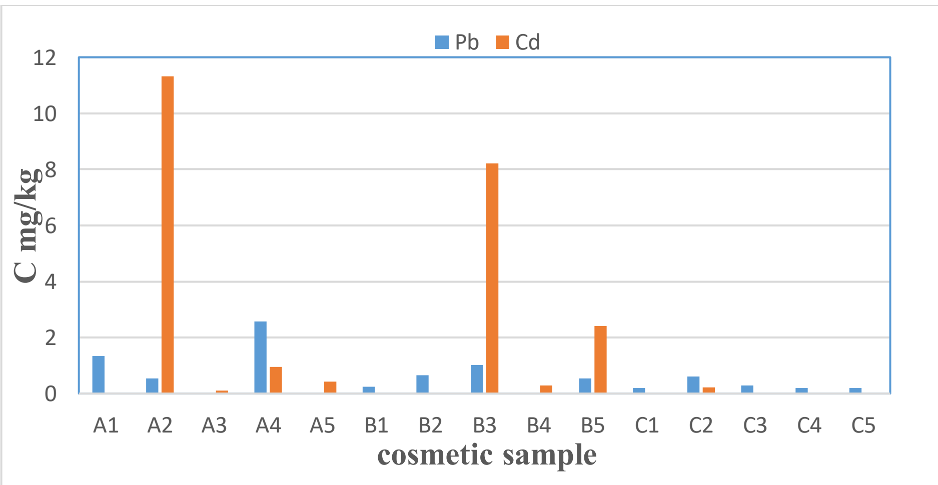

Fig. 1. a: Concentration of pb and cd of studied cosmetics samples

Microbiology Analysis of Cosmetics Samples:
All of the cosmetic samples were microbiologically analyzed and the result showed that no bacterial or fungal growth in any of the study samples.

Discussion:
In this study, as shown table 2. fifteen individual cosmetic products were tested to determine the concentration of some heavy metals. The products were sold by a distinct seven companies, such as Foundation cream from: Max Facter, Bourjois, Fina lTough, Mac and Dermlys (sun screen), Blusher from: Sevencool, Flormar, Gosh, MayBelline and BBoose Insta glow, and Face powder from: Danni, Bourjois, Sephora, Flomar and Huda beauty. Although EU regulation has suggested that the concentration of some heavy metals, such as chromium, in colour additive cosmetics should be <1.0 mg/kg,[17]. there were two samples with chromium concentration higher than EU standard in cosmetic products. The presence of chromium in the body facilitates the entry of glucose into cell [20]. However, exposure to high levels of chromium has been linked to kidney and lung damage and other cancers. Chromium is also linked to skin effects such as eczema and other inflammations of the skin [23].
Zinc was detected in eight samples. Mahmood *et al*. reported that zinc oxide was probably used in face powder because of its powerful natural sunblock property [27-29]. Furthermore, zinc is necessary for oxygen metabolism and mitochondrial function [4].
According to international Standards for lead metals, all study samples were considered free of lead contamination, but eight samples were found to be contaminated with cadmium according to the WHO. And only three sample were contaminated according to health Canada, and just only one foundation cream sample was contaminated according to the EU as shown in table 3.
The toxic metals, such as lead and cadmium, were detected in some samples. However, the WHO sets maximum limits at 10.0 and 0.3 mg/kg, for lead and cadmium in cosmetic products, respectively [23], and 10.0 and 3.0 mg/kg, for lead and cadmium in cosmetic products, respectively [25]. Figure 1a. shows the comparison of the levels of lead and cadmium that were detected in the investigated samples with the maximum allowed limits of these metals recommended by the WHO in cosmetics. Figure 1a shows that there was no cosmetic sample that had a content of lead higher than the maximum level recommended by the WHO. In fact, but the contents of cadmium in 3 samples were above the allowed maximum limit, recommended by the WHO for cadmium in studied cosmetics samples. Figure 1b. shows the comparison of the levels of both heavy metals such as Cr^{2+}, Zn^{2+} and Mn^{2+}, that there was all the level of metals under the normal concentration and it which might be no of the major public health hazards, where the highest reading of zinc was recorded for each of C1 and C2 of the face powder cosmetics samples.

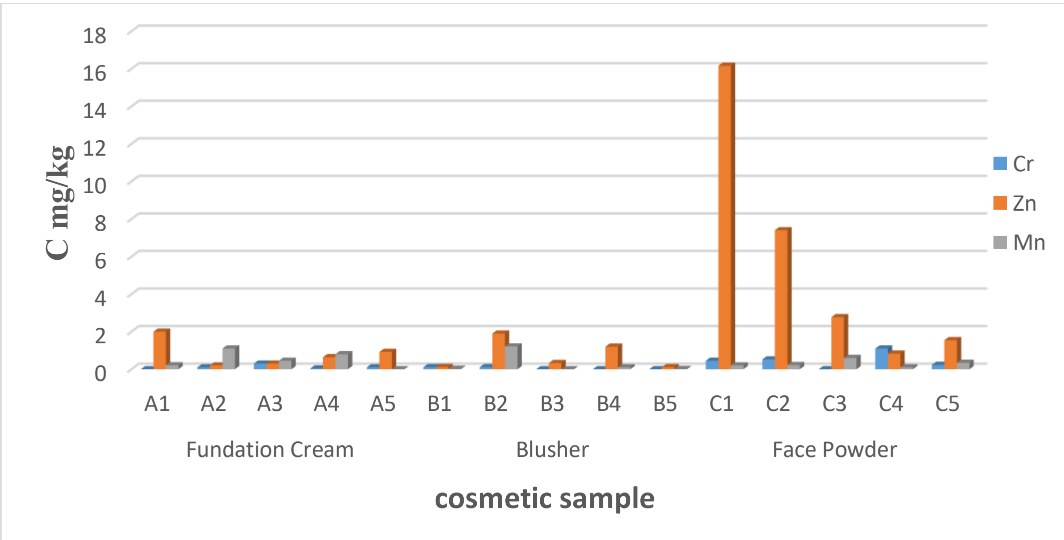

Fig. 1.b: Concentration of some heavy metals of studied cosmetics samples

Conclusion:
In this study, the presence of trace metals such as lead, cadmium, chromium, manganese and zinc elements in some cosmetic products sold in Benghazi markets in Libya. The results of this study showed that the concentration of cadmium in investigated cosmetic samples such as foundation cream and blusher are high which might be a

one of the major public health hazards especially for women. The high levels of cadmium in 3 samples tested cosmetic samples can cause lead poisoning or impregnation of regular cosmetic products users. In addition, our results indicate a need for establishing safe intake values of heavy metals in cosmetic products and point out the importance of their analysis before they reach the consumer. Concerning the microbial contamination screening, for cosmetics products analyzed in this study, the results showed that there was no biological growth.

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