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Research Article

Health Risk Assessment of Some Heavy Metals in Cosmetics in Common Use

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ABSTRACT

There have been a number of recent reports discussing the presence of heavy metals in cosmetics. Therefore, the present study was planned to assess the health risk due to exposure to heavy metals in various brands of cosmetics sold in low price stores in Alexandria market, Egypt. Nine heavy metal contents were measured in 20 different cosmetics commonly used in Alexandria using the atomic absorption spectrometry and cold vapor unit for Hg after wet digestion procedure. The mean concentrations of metals in these facial cosmetics ranged from ND-80.8 µg/g Cd, 81.7-159.1 µg/g Pb, 38.9-67.2 µg/g Cr, 17.4 -41.5 µg/g Ni, 8.9-32 µg/g Cu, ND-0.025 µg/g Hg, 255.8-1192 µg/g Fe, 4.7-314 µg/g Mn, and from 5.72-110.8 µg/g Zn. The concentrations of Ni, Cr, Pb and Cd were above the suggested safe limit for skin protection. The systemic exposure dosage (SED) values for these metals acquired from the personal care products were below their respective recommended daily intake (RDI) values. The margin of safety values obtained were greater than 100 which indicated that the concentrations of metals investigated in these facial cosmetic exert a no risk associated with their occurrence in these products. The maximum value of oral cancer risk was detected in cream and the minimum value in eye pencils.

Key words: Heavy metals, Health risk assessment, Cosmetic products.

INTRODUCTION

The use of cosmetics as part of routine body care is as old as man. The demand for cosmetic products from around the world has increased rapidly due to the growing awareness of the need to beautify the human body [1] and the sharp rise in product advertisements in the media [2]. Despite the high global demand for cosmetic products, the safety of these products is of great concern and has attracted the attention of researchers, toxicologists and regulators, with the common objective of ensuring the safety levels of ingredients in products [3,4].

Cosmetics have been considered by many dermatologists often more serious than useful. They may contain more than 20,000 ingredients that are related to many diseases such as eczemas, irritant contact dermatitis cancer, birth defects, development and reproductive system damage. To know these poisonous effects completely banned the presence of nine ingredients including the colors of coal tar, formaldehyde, glycol ethers, chromium, lead, mercury, phenylenediamine, Parabens and phthalates in cosmetics [5].

There are variable types of personal care products, PCP, between lipstick and lip gloss (used to color the lips); Mascara, eyes and eye shadows (used to color the eyelids); blusher and powder (used to color your face, reduce and eliminate defects); nail polish (used to color nails and feet) and different types of moisturizing and lightening / toning creams. Heavy metals, HM, are widely used in dyed makeup products. Cosmetics are one of the most severe reasons to release HM [5,6].

Chromium hydroxide [$Cr_2O(OH)_4$] and chromium oxide [Cr_2O_3] are used as coloring agents in cosmetic products such as eye shadow [7,8]. Eye cosmetics such as eye pencil have been identified as a suspected source of Pb exposure to the ocular system in a number of adults and children. The use of leaded eye cosmetics have been observed to be strongly correlated with elevated blood Pb levels [9,10]. Skin whitening creams containing hydroquinone, corticosteroid and mercury [12]. The use of Cd in cosmetics products is due to its color property and it has been used as a color pigment in many industries. The Cd sulfide is used for the yellow color, while, by adding increasing amounts of selenium, colors ranging from orange to practically black (the color of Cd selenide) can be produced. Cadmium yellow is sometimes mixed with viridian (Cr(III)oxide) to give a light green mixture called cadmium green [13]. Cd and its compounds are considered human carcinogens [14-17]. Egypt follows the European Union and the EU has not set any specific legal limits for ubiquitous traces of heavy metals in cosmetic ingredients.

Studies on the concentrations of metals in facial cosmetic products in Egypt and all over the world have been documented in the literature [1-4,18-29]. However, although most of the studies established the levels of metals in some facial cosmetic products, they paid little to risk assessment. The aim of this study is to focus on the assessment of health risk due to the measured concentration of some heavy metals in cosmetics commonly used in Alexandria, Egypt.

MATERIAL AND METHODS

Sampling

Collection of samples of different brands of facial cosmetics (n = 20) were collected from cosmetics shops in Alexandria City in Egypt. The cosmetic samples were popular brands, some of which were produced locally and others imported. Most of the imported products examined were from Germany, China, India, France, and United Arab of Emirates. The choice of brands was carefully made to reflect the types used. The facial cosmetics were classified into five broad groups, namely, (1) lipsticks, LS, (2) eye shadows, E, (3) eye pencils, K, (4) face powders, PP, and (5) moisturizing creams, CC. The samples were stored under conditions similar to those of the retail shops until the analysis was completed.

Chemicals and standards

All reagents, nitric acid (HNO_3 69% v/v), hydrochloric acid (HCl 37% v/v) hydrogen peroxide (H_2O_2 30% v/v), Potassium permanganate ($KMnO_4$) and Hydroxyl amine were purchased from ADWIC obtained from El-Gomhouria Company, Egypt. Hydrofluoric acid (HF 40% v/v) were purchased from SDFCL, India. The calibration standards were prepared by diluting 1000 mg L^{-1} commercial standards of Cd, Pb, Ni, Cr, Cu, Co, Zn, Fe, Mn and Hg (Merck, Darmstadt, Germany), and adding 2 drops of (HNO_3 69% v/v).

Sample preparation

Solid samples were dried in an oven at 105°C for 2h to remove moisture and to obtain a constant weight and then cooled in desiccators. Creamy samples liable to charring were dried at 70–80°C. Also the moisture percentage was measured using infra-red moisture determination instrument Japanese made [19].

Sample digestion for all metals except Pb and Hg

A modified method of Iwegbue et al, 2016, [18] was adopted. A mass of 1.0 g of each sample was placed into a bottle of 100 ml and treated with 20 mL of concentrated nitric acid, 10 mL of hydrochloric acid and 5 mL of hydrogen peroxide. The samples were covered and left to stand overnight. The samples were heated to 125°C under open system on hot plate until the white fumes started evolving, which showed the completion of digestion process. The clear supernatant solutions were allowed to cool, filtered and made up to 50 mL with distilled water then adding 0.25 mol L^{-1} HNO_3. Three blanks were prepared in a similar way, but omitting the samples.

Sample digestion for lead

A modified method of Vlope et al, 2012, [20] was used. 1 g of sample were added to 5mL of 67% HNO3 and 1mL of 40% HF into Teflon vessel and heated up to 150° C for 2½ h . Then the acid digest was allowed to cool and filtered into a 50 mL volumetric flask, using Whatman filter paper and made up to mark.

Sample digestion for mercury

A method of US EPA, 2011, [30] Hg was used. 2gm of sample was put in beaker 100ml. 20ml HNO_3 and 20ml H_2SO_4 were added. 7ml of 5% $KMnO_4$ was added and beaker was put on water bath at 60°C for 2 hours. Then beaker was cooled and 3ml of 12% hydroxylamine solution was added to reduce the $KMnO_4$. Solution was filtered and made up to 50ml with distilled water and 2 drops of 3% HCl was added.

Analysis

The heavy metal contents of chromium (Cr), copper (Cu), iron (Fe), lead (Pb), zinc(Zn), magnesium(Mg), manganese (Mn) and nickel (Ni) were determined according to the standard method of AOAC (2016) [31]. Determination was performed using Atomic Absorption Spectroscopy (AAS), S Series AA Spectrometer and Thermo SCIENTIFIC. Hg was measured using cold vapour unit. All sample analyses in this study were performed in triplicates and the results were reported as mean values under condition shown in Table 1. The obtained data were subjected to statistical analysis via Microsoft Office Excel 2010.

Table 1: Instrumental analytical conditions of investigated elements

Condition	Cu	Cr	Hg	Zn	Fe	Cd	Ni	Pb	Mn
Wave length (nm)	324.8	357.9	253.7	213.9	248.3	228.8	232	217	279.5
Lamp current	75	100	75	75	75	50	75	75	75
Fuel flow L/min	1.1	4.2	No heating	1.2	0.9	1.2	0.9	1.1	1
Burner height mm	7	8	17	7	7	7	7	7	7
Air flow rate	3	3	-	3	3	3	3	3	3
Band pass (nm)	0.5	0.5	0.5	0.2	0.2	0.5	0.2	0.5	0.2

Assessment of Health Risk

Non-cancer risk; Safety evaluation of facial cosmetic products and margin of safety

The risk of human exposure to metallic impurities in these facial cosmetic products can be assessed by making use of the uncertainty factor called the Margin of Safety (MoS).The MoS is the ratio of the lowest no observed adverse effect level (NOAEL) value of the cosmetic substance under study to its estimated systemic exposure dosage (SED). The systemic availability of a cosmetic substance is estimated by taking into consideration the amount of the finished product applied to the skin per day, the concentration of metals in the cosmetic product under study, the dermal absorption of the metal and a human body weight value. The systemic exposure dosage (SED) is given by the formula: MoS = NOAEL / SED/ SED ($\mu g/kg$ BW day^{-1}) = $\times 10^{-3}$ Where Cs is the concentration of metal in the facial cosmetic product (mg kg−1) and SSA is the skin surface area onto which the products are applied. The applied surface areas (in cm^2) for the different facial cosmetic products were 4.8, 4.8, 563, 24, 3.2 and 565 for lipsticks, face powder, eye shadow, eye pencil and cream respectively. AA is the amount of facial cosmetic product applied per day. The estimated daily amounts (in g) applied were 0.057, 0.51, 0.02, 0.005 and 1.54 for lipstick, face powder, eye shadow, eye pencil and cream respectively. RF is the retention factor (1.0 for leave-on cosmetic products); F is the frequency of application per day were 2.14, 2 for cream and eye shadow/eye pencil/lip stick/ powder; BF is the bio accessibility factor; 10^{-3} is the unit conversion factor; and BW is the body weight (kg). A default body weight of 70 kg was used in this study. The values of AA, SSA, and RF used in this study were the standard values established by the Scientific Committee on Consumer Safety [32].
The NOAEL values were obtained from the oral reference doses (RFDs). The latter are "an estimate of the daily exposure to the human population (including sensitive sub-groups) that is likely to be without an appreciable risk of deleterious effects during lifetime". For the studied metals the NOAEL values were calculated by using the relationship, NOAEL = RFD × UF × MF, where UF and MF are the uncertainty factor (reflecting the overall confidence in the various data sets) and the modifying factor (based on the scientific judgment used) respectively. In this case the default values of UF and MF were 100 and 1. The RFDs (in mg $kg^{-1} day^{-1}$) used were Pb (4×10^{-3}), Cd (1×10^{-3}), Cr (3×10^{-3}), Co (3×10^{-4}), (Zn (3.0×10^{-1}), Fe (7.0×10^{-1}), Cu (4.0×10^{-2}), Mn (1.4×10^{-1}), Ni (2×10^{-2}) and Hg (3×10^{-4}) (US EPA 1989, 2011).
NOAEL = RFD × UF × MF
World Health Organization, WHO, proposed a minimum value for the MoS of 100 and it is generally accepted that it should at least be 100 to conclude that a substance is safe for use.

Hazardous Quotient (HQ)

Hazardous Quotient (HQ) for consumers through the consumption of contaminated cosmetics was assessed by the ratio of Systemic Daily Exposure Dose (SED) to the oral reference dose (RfD) for each metal. If the value of HQ is less than 1, then the exposed local population (consumers) is said to be safe, if HQ is equal to or higher than 1, is considered as not safe for human health, therefore potential health risk occurred, and related interventions and protective measurements should be taken. Where, RfD is the oral reference doses. RfD is an estimate of a daily dermal exposure for the human population, which does not cause deleterious effects during a lifetime. (US EPA, 2011; Liu et al., 2013)

Hazardous Index (HI)

To estimate the risk to human health due to the exposure to the nine heavy metals, the hazard index (HI) has been developed. Hazard index is the sum of the hazard quotients for all heavy metals, which was calculated by:

$$HI = \sum HQ = HQ_{Hg}+HQ_{Cr}+HQ_{Cu}+HQ_{Fe}+HQ_{Pb}+HQ_{Zn}+HQ_{Mg}+HQ_{Mn}+HQ_{Ni}$$

Cancer Risk

Carcinogenic risk is usually evaluated for carcinogens; the slope factor represents an estimated upper bound of the probability of an individual's carcinogenic response per unit intake dose of a chemical over an average lifetime. The slope factor for Pb 0.0085 mg/kg/day multiplied by the chronic daily intake value gives a maximum probability that a receptor will develop cancer from exposure to a chemical over a life time. HI values of heavy metals for all plants were between1 to 5 (one to five) by US EPA, (2011) indicated that there was no risk from the intake of cosmetics.

$$\text{Risk} = \text{SED} \times \text{SF}$$

Where; Risk is a unit less probability of an individual developing cancer over a lifetime, and SF is the carcinogenicity slope factor (mg/kg/day).

RESULTS AND DISCUSSION

Samples of a variety of commercially available lipsticks, face powder, eye pencil, eye shadow and skin creams were purchased and prepared in duplicate. The percentage of moisture content (Figure 1) of PCPs shows that creams have the highest water content followed by eye pencils, lip sticks, powders and eye shadows. Results are in agreement with those reported by Iwegbue et al, 2016, [18]. Wet digestion method has been applied in several analyses of cosmetic samples according to literature [4,18,19]. Small amount of HF in the digestion: to ensure better recovery of all the metal including that which might be protected from other acid attack by silica particle. HF is better for recovery of lead due to Pb enclosed in silica particles [18]. The variation of heavy metal concentrations (µg/g) among different types of cosmetics are presented in Table 2.

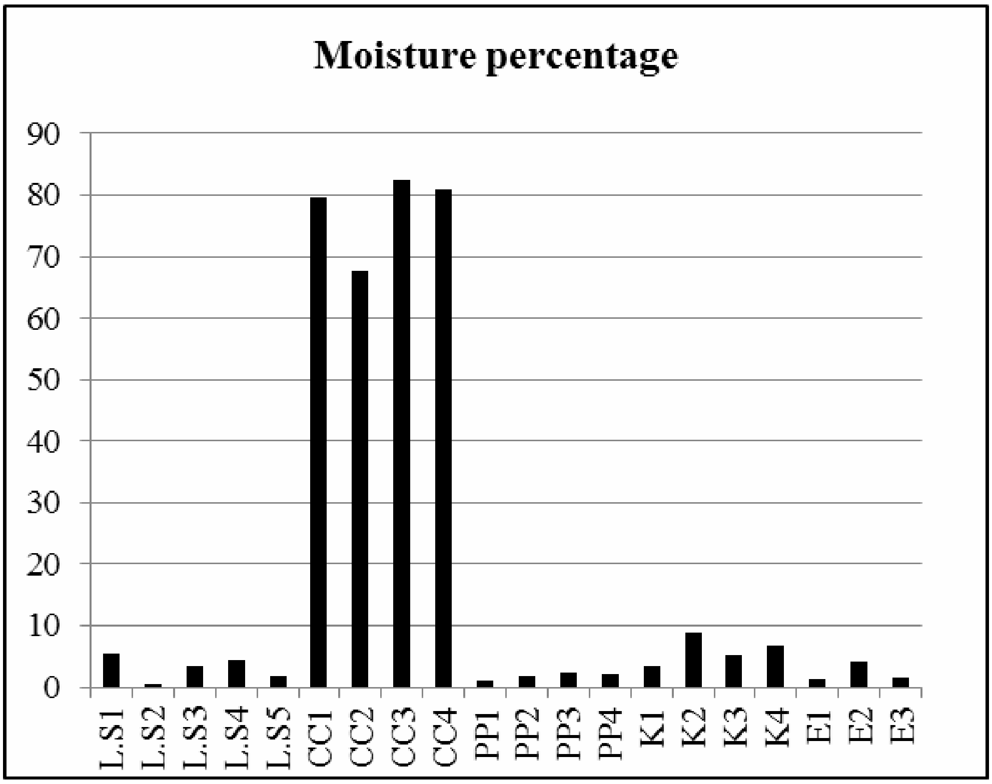

Figure 1: Moisture contents in PCPs samples. LS; lips stick, CC; cream, PP; powder, K; eye pencil, E; eye shadow.

Table 2: Concentrations (µg/g) of selected heavy metals in some cosmetics samples commonly used in Egypt

Sample Codes	Cd	Cr	Ni	Cu	Mn	Fe	Zn	Pb	Hg
E1	1.53±0.01	43.97±0.28	32.05±1.48	6.68±0.54	61.6±0.14	1332.21±0.17	258.26±3.35	103.04±0.69	0.075±0.09
E2	2.18±0.01	41.95±0.06	27.77±0.2	56.77±0.01	165.57±2.02	1008.52±6.97	32.01±4.23	140.57±0.38	ND
E3	0.4±0.03	30.8±0.72	19.88±1.24	8.77±1.74	42.2±0.07	1030.97±2.79	318.76±0.65	81.02±0.05	ND
K1	0.07±0.02	47±4.24	40.86±1.22	26.25±1.36	299.35±14	1271.5±7.78	82.29±1.08	120.45±1.75	0.0017
K2	0.09±0.01	34.75±0.34	41.4±0.71	73.37±0.11	324.31±0.48	1261.5±3.54	55.93±0.65	201.15±1.63	ND
K3	1.93±0.07	41.62±0.04	30.73±1.04	3.49±0.07	232.41±0.17	1281.5±9.64	7.98±0.3	218.35±1.98	ND
K4	0.33±0.04	34.36±0.51	53.38±1.95	25.44	401.13±1.6	1254±1.8	52.15±1.63	96.37±0.03	ND
PP1	ND	32.51±15.55	22.99±4.39	3.5±1.06	81±4.24	1325±14.14	16.12±0.1	80.66±1.48	0.0025
PP2	ND	49.76±7.12	43.81±0.92	5.35±0.05	27.96±1.46	1160.95±24	129.51±14.2	280.9±0.85	ND
PP3	ND	37.37±3.47	23.86±0.85	2.4±1.13	21.5±2.73	1320±7.07	242.13±0.64	88.32±2.56	ND
PP4	0.22±0.08	51.98±0.02	43.19±4.79	58.88±3.66	157.43±10.6	963.49±5.35	55.26±0.37	162.59±9.86	ND
CC1	ND	29±0.94	11.43±1.18	12.96±1.13	3.71±0.28	157.71±10.4	10.22±0.06	75.49±0.38	ND
CC2	ND	36.68±1.3	10.74±0.67	6.2±0.07	3.51±0.5	163.8±2.45	3.88±0.01	110.85±5.9	ND
CC3	0.08±0.02	29.15±0.04	9.63±0.35	28.54±0.46	3.55±0.31	166.96±16.6	3.62±0.06	129.26±0.13	ND
CC4	ND	65.27±0.07	37.94±1.75	2.36±0.28	8.12±0.18	534.78±26.7	5.16±0.84	11.54±0.17	ND
L.s1	ND	51.13±5.85	24.49±0.99	21.72±0.02	32±0.47	1290±26.1	12.32±0.85	195.25±5.23	0.022
L.s2	0.85±0.28	75.87±1.73	28.89±2.4	5.42±0.03	24.84±0.09	1382±31.2	37.27±3.09	109.66±0.42	ND
L.s3	403±12.5	70.78±0.38	29.21±0.55	6.7±0.45	16.43±1.29	1357.2±19.4	216.53±7.07	198.49±4.32	0.0077
L.s4	ND	27.63±0.06	9.16±0.09	1.86±0.22	8.93±0.01	951.56±5.93	3.64±0.06	111.35±1.85	ND
L.s5	0.41±0.06	110.72±6.13	74.46±0.78	9.1±0.24	20.78±0.13	804.3±2.05	15.61±0.09	121.43±0.32	ND

ND*; Not Detected.

The variations of heavy metal concentrations (µg/g) in PCPs collected from Alexandria were sorted in the following order Fe>Pb>Mn>Zn>Cr>Ni>Cu>Cd, as illustrated in Figure 2. Where the dominant elements in PCPs were Fe, Pb, Mn, Cr, Ni, Zn and Cu, and the minimum concentrations were noted for Cd and Hg.

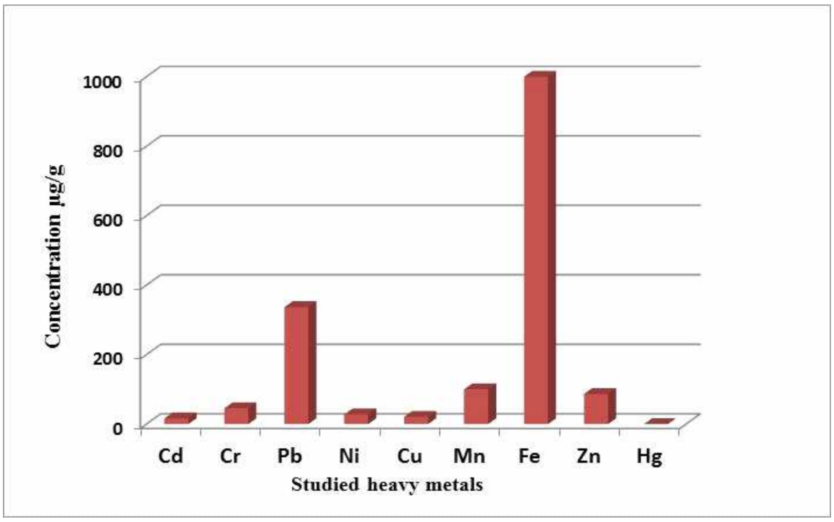

Figure 2: Heavy metals concentrations in the studied PCPs.

The values of Cd ranged from 0.4 to 2.18µg/g in eye shadow samples and 0.07 to 1.93µg/g in eye pencil. In lip stick the concentration ranged from ND to 403µg/g, where in powder was ND to 0.22 µg/g and in cream was ND to 0.08µg/g. Result obtained in this study were compared with the available international permissible limits 5ppm for FDA, Italy and Germany and 3ppm for Health Canada. Most of samples in this study were below the permissible limits, are unlikely to present any health risk. Only one sample LS3 imported from china above the limits and may cause harm. In Products available in Nigeria locally produced or imported, high levels of cadmium in some PCPs samples were reported [4,18,19]. While in other studies [3,24], a lower quantity of Cd was found. Also eye shadows and mascara sold in Saudi Arabia had low concentrations of Cd; 0.014-0.266 µg/g and 0.002-0.035 µg/g, respectively [22]. The order of cadmium concentrations in the samples were lip sticks > eye shadows > eye pencils > face powder and creams. Chronic exposure to low levels of Cd can also cause the bones to become fragile and break easily. This assessment was based on carcinogenic effects on lungs after inhalation, but tumors in other organs (prostate and kidney) have been observed. The use of Cd in cosmetic products is due to its color property and has been used as color pigment in many industries [33].

Chromium concentrations ranged from 27.63 to 110.72µg/g in lip stick, 29 to 65.57µg/g in cream samples, 32.51 to 51.98µg/g in powder samples, 47 to 34.36 µg/g in eye pencils, 30.8 to 43.97 µg/g in eye shadow samples. High concentrations of chromium were found in LS5, magical lip stick, imported from West Africa whose colour is green and give red colours with use. Comparing with results reported by Iwegbue et al, 2016, [18] the obtained results are almost similar. Very high concentration of Cr was observed in eye shadow and mascara in Saudi Arabia [22]. Eye shadows imported in the Egyptian market were found to contain very high amounts of Cr (16.05–29,800 µg/g); the same authors found elevated Cr also in Egyptian locally-made products as face powders (2.94–22.65 µg/g) [26]. Concentration of chromium was variable from traces to very high values [20]. The high concentration of Cr is due to the use of Cr-containing colouring agents. The order of chromium concentrations in the samples were lip sticks > powder > cream > eye pencil and eye shadows. Eye shadow is an example of a cosmetic product in which significant amounts of colourants are used. Exposure to Cr can cause skin ulcers, and severe redness and swelling of the skin. There are no international guidelines or limits for Cr and Ni in cosmetic products, however, several studies have shown that the presence of irritants, and/or following repeated exposures to Ni and Cr subjects rarely react to levels below 10 µg/g. For this reason, Basketter et al, 2003, [34] recommended that consumer products should not contain more than 5µg/g of Cr and Ni, and for better health protection levels should not exceed 1µg/g.

The mean concentrations of Ni ranged from 9.16 to 74.46µg/g in lip stick samples, 9.63 to 37.94µg/g in creams, 22.99 to 43.81µg/g in powder, 30.73 to 53.38µg/g in eye pencil samples and 19.88 to 32.05µg/g in eye shadows. Concentrations were ordered as eye pencils > face powders > lip sticks > eye shadows and creams. Comparing results with those of Iwegbue et al, 2016, [18] they were almost similar. Eye make-up samples sold in Nigeria showed very high Ni levels with mean values in eye liners of 9.2µg/g, in eye pencils of 13.4µg/g and in lipstick of 14.6µg/g [4]. On the contrary, Adepoju-Bello et al [35] for products of lipsticks, lip glosses and skin lightening creams sold in Nigeria presented very low mean level of Ni (i.e., 0.05µg /g). Omenka et al, 2016, [19] reported a high concentration of Ni in powder samples sold in Nigeria. In addition Nnorom et al [4] stated a high concentration of Ni in eyeliner and eye pencil samples. Also, ED, Canada [28] stated Ni concentration from traces to high concentration (0.3 to 230µg/g) in foundation, concealer, powder, blushes, mascara and bronzer. A Ni concentration of about 0.5µg/g is sufficient to cause contact dermatitis in an already irritated skin. Contact allergies associated with Ni exposure arise due to the ability of nickel to bind to amino acid residues to form Ni complexed proteins. Nickel represents the main cause of contact dermatitis and minimal amount of other toxic metals can trigger pre-existing allergy. Nickel dermatitis produces erythematic and eczema of the hands and other areas of the skin that is in contact with nickel.

Cu maximum values in lip stick, creams, powders, eye pencil and eye shadow were 21.72, 28.54, 58.88, 73.37, and 56.77µg/g, respectively while the minimum values were 1.86, 2.36, 2.4, 3.49, and 6.68, respectively. Highest concentration of copper was observed in eye pencil (K2) imported from china. Order of Cu concentration in samples was eye pencils > eye shadows > face powder> cream and lip stick. Higher concentrations of Cu in some cosmetic samples could be due to the fact that copper containing compounds might have been used as pigments in these types of facial cosmetics [18].

Range of mean concentrations of Mn were 8.93 to 24.84µg/g, 3.51 to 8.12µg/g, 21.5 to 157.43µg/g, 232 to 401.13µg/g and 42.2 to 165.57µg/g in lip stick, creams, powder, eye pencil and eye shadows, respectively. Order of Mn concentration in cosmetic samples was eye pencils > eye shadows > face powder > lip stick and cream. Although Cu and Mn are rare skin sensitizers, there were cases reported with increased menstrual blood loss and pain as a result of exposure to Cu from widely used intra-uterine devices (IUDs) or immune reactions due to exposure to Cu from handling of euro coins, while the risk of sensitization for both Cu and Mn has been reported from the use of prosthetic materials in dentistry [18].

Fe was relatively high in all cosmetics samples. Ranges of mean concentrations were 804.3 to 1382µg/g in lip stick samples, 157.71 to 534.78µg/g in cream samples, 963.49 to 1325µg/g in powder samples, 1254 to 1281.5µg/g in eye pencils, and 1008.52 to 1332.21µg/g in eye shadows. Fe concentrations in these samples were higher than any element studied. Exposure to small amounts of Fe from cosmetic products may cause cellular death or colorectal cancer as a result of cumulative effects. Highest concentration of Fe found in lip stick sample LS2 imported from China this is due to iron oxide pigment in lip stick. The order of Iron concentrations in the samples were eye pencil > powder > lip stick > eye shadows and creams [18].

Zn, Fe, Mn and Cu are dominant elements in this study. Results were compared to previous results [18,19] and were almost similar Also eye shadows and mascara sold in Saudi Arabia had a high concentration of Mn [22]. Al-Qutob et al and Sani et al [23,24] reported Mn concentration in cosmetic samples.

Pb concentrations in this study were relatively high. The mean concentration range was 109.66 to 195.25µg/g in lip stick samples, 11.54 to 129.26µg/g in cream samples, 280.9 to 80.66 in powder samples, 96.37 to 218.35µg/g in eye pencil, and 81.02 to 140.57µg/g in eye shadows. Highest concentration of Pb was observed in eye pencil samples. Order of Pb concentration in all samples was eye pencils > face powder > lip stick > eye shadow and cream. A high concentration of Pb was observed in all samples when compared with international guidelines of FDA, Italy and Germany (20µg/g) and Health Canada (10µg/g). Results are in agreement with those reported by Iwegbue et al [18]. The high lead levels in make-up for eyes appear to have a significant Pb exposure. Sample purchased in Nigeria contained a high level of Pb (9.6-322.5µg/g) and (3.3-33.8µg/g) in eyeliner and eye pencil, respectively. In addition to, face powder ranges from 5.9 to 3399.9µg/g and the blush samples ranges from 12.1 to 378.0µg/g. In fact, eye cosmetic is composed mainly of galena (PbS), amorphous carbon, zincite (ZnO), sassolite (H_3BO_3), minium (Pb_3O_4), magnetite (Fe_3O_4), goethite (FeO(OH)), cuprite (Cu_2O), and talc ($Mg_3Si_4O_{10}(OH)_2$). Because of its composition, kohl is considered by the US Food and Drug Administration [5] as unsafe for use and as an illegal substance to be imported or sold in the United States while, in other countries such as Egypt, it is still largely sold in markets without any legal control.

A wide concentration range of Pb was found in various types of cosmetics imported from china, India, Saudi Arabia and some studies observed that products coming from China were the most contaminated [9,20,27]. Al-Saleh et al [27] found high levels of Pb ranges from 0.42 to 58.7µg/g and 0.27 to 3760µg/g in eye shadows and lip stick, respectively imported from China, Italy, USA. High levels of Pb were observed in Kohl that is ordinary composed of galena (PbS) and silver galena (Pb_2SO_4) [29]. Ullah et al [1]found a high lead levels in Kohl samples imported from Pakistan with ranges from 2.774 to 1071µg/g. High concentration of Pb in eye shadows samples from Italy, China, USA with a range of 0.25 to 81.5µg/g [20].
Hg concentrations were relatively low the maximum was detected in eye shadow 0.075µg/g, taking into consideration that all the samples in this study under the international guidelines. All the samples in this study had a mercury concentration below the international guidelines of 1ppm for FDA, Italy and Germany and 3ppm for Health Canada. Mercury is a volatile element and is harmful to the skin when used in an effort to lighten the skin. However, chronic exposure of the body to mercury at very low concentration can cause long-lasting neurological and kidney impairment [36]. Mercury in bleaching preparations can be absorbed through the skin and accumulates in body organs giving rise to severe toxicity [37]. The order of mercury concentrations in the samples were eye shadows > lip stick > eye pencil >powder and cream. Comparing with application note published in America results almost similar where Hg values in lip stick, nail polish and cream range from ND to 0.0125µg/g, and ND to 0.192µg/g and ND, respectively. In addition, Zhang et al [21] found in a cream elevated amount of Hg–ammonium chloride (250µg/g), a very toxic substance even at much lower concentrations. Murphy et al [25] found very different Hg levels in 19 skin creams sold in Cambodia. In 10 samples the metal was below 0.5 µg /g, while in the remaining 9 samples Hg ranged from 19 to 12590µg/g. In addition, the same authors reported a significant association between Hg contents and creams labeled ‘‘for export only’’.

Exposure and risk assessment of PCPs

The risk assessment was calculated for both dermal and oral exposure pathways. The mean concentrations of heavy metals were used for calculation of exposure health risk. Oral pathway seems to be the highest risk of using cosmetics (Italy). Oral and dermal route of exposure appear to be equal in risk for all elements. HQ and Risk is also calculated. Results are in agreement with those reported by Iwegbue et al [18] who estimated margins of safety of metals in these cosmetic products were greater than the minimum value of 100 proposed by the WHO to conclude that a substance is unsafe for use, although, some metals can buildup in the human body over time and cause adverse health effects.

Table 3: Systemic Exposure dosage and margin of safety of metals in facial cosmetic

	Cd	Cr	Pb	Ni	Cu	Mn	Fe	Zn	Hg
				Systemic Exposure Dosage					
Lip Stick	6E-07	5E-07	1E-06	3E-07	7E-08	2E-07	9E-06	4E-07	5E-11
Cream	1E-07	0.0011	0.0022	0.0005	0.0003	0.0001	0.0068	0.0002	0
Eye Pencil	3E-10	2E-08	7E-08	2E-08	1E-08	1E-07	5.8E-07	2E-08	2E-13
Face Powder	5E-07	0.0004	0.0013	0.0003	0.0001	0.0006	0.00978	0.0009	5E-09
Eye shadow	2E-08	5E-07	1E-06	4E-07	3E-07	1E-06	1.5E-05	3E-06	3E-10
				Margin Of Safety					
Lip Stick	158220	570868	347535	8E+06	6E+07	9E+07	7739486	7E+07	6E+08
Cream	1E+06	281.78	183.87	4312.4	11951	111448	10287.1	197170	0
Eye Pencil	4E+08	2E+07	6E+06	1E+08	3E+08	1E+08	1.2E+08	1E+09	2E+11
Face Powder	221629	852.32	318.44	7285.5	27810	23711	7156.16	33018	6E+06
Eye shadow	5E+06	562243	269538	5E+06	1E+07	1E+07	4541478	1E+07	9E+07

The estimated SED (µg kg^{-1} dw day^{-1}) and MOS of metals from the use of these facial cosmetic products are displayed in Table 3. The SED of Cd and the SED of Pb from the use of these facial cosmetic products ranged from 7E-08 to 0.002 µg kg^{-1}bw day^{-1}.m and 3E-10 to 6E-07 µg kg^{-1}bw day^{-1} respectively. The estimated SED values of Cr obtained from the use of these facial cosmetic products ranged between 2E-08 and 0.001 µg kg^{-1}bw day^{-1}, while the SED of Ni ranged between 2E-08 and 5E-04 µg kg^{-1}bw day^{-1}. The systemic exposure dosage of Cu from the use of these facial cosmetic products ranged from 1E-08 to 3E-04 µg kg^{-1}bw day^{-1}. The SEDs values of Hg obtained from the use of our cosmetic products varied from ND to 5E-09 µg kg^{-1}bw day^{-1}. The estimated SEDs of Fe, Mn and Zn from application of these facial cosmetic products are below their respective recommended intake values. The systemic exposure dosage of Fe, Mn, and Zn from the use of these facial cosmetic products ranged from 6E-07 to 0.01, 1E-07 to 6E-04, and 2E-08 to 9E-04 µg kg^{-1}bw day^{-1}, respectively. The estimated margin of safety for metals in these facial cosmetic products was greater than the proposed value of 100 set by the WHO. Eye pencils have highest MoS values compared with other facial cosmetic products investigated. The MoS values indicate that there is little risk associated with the concentrations of metals in these products.

Table 4 illustrates HQs and HI of oral and dermal pathways in the PCPs samples. In case of each cosmetics sample, HQ value was lower than 1 indicated that the overall risks in both exposure pathways are within safe level. A max HQ values to Cd, Cr, Pb, Ni, Cu, Mn, Fe, Zn and Hg are 2E-04, 0.355, 0.544, 0.023, 0.008, 0.004, 0.0145, 0.003, and 2E-05, respectively, indicating that there is no risk of carcinogenic effects. HI to lip stick, cream, eye pencil, face powder and eye shadow are 7E-04, 0.941, 3E-05, 0.47 and 6E-04, respectively. Results are in agreement with those reported previously [18,38].

Table 4: Hazardous quotient, HQ, and hazardous index, HI for the measured heavy metals

PCPs	Cd	Cr	Pb	Ni	Cu	Mn	Fe	Zn	Hg	HI
	HQ									
Lip Stick	0.0002	0.0002	0.0003	1E-05	2E-06	1E-06	1E-05	1E-06	2E-07	**7E-04**
Cream	3E-05	0.3549	0.5439	0.0232	0.0084	0.0009	0.0097	0.0005	0	**0.941**
Eye Pencil	9E-08	6E-06	2E-05	1E-06	4E-07	1E-06	8E-07	8E-08	6E-10	**3E-05**
Face Powder	0.0002	0.1173	0.314	0.0137	0.0036	0.0042	0.014	0.003	2E-05	**0.47**
Eye shadow	6E-06	0.0002	0.0004	2E-05	8E-06	9E-06	2E-05	9E-06	1E-06	**6E-04**

Table 5 illustrates the risk due to oral cancer and cancer risk index. On the other hand, carcinogenic metal risk assessment caused by Pb was calculated on basis of oral exposure pathway achieved that the maximum value of oral cancer risk was 2E-05 in cream and the minimum value was 6E-10 in eye pencils. In addition to the maximum value of cancer risk index 18.49 chances per million was observed in creams.

Table 5: Oral cancer and cancer risk index

PCPs	HM	Oral cancer	Cancer risk index
Lip stick	**Pb**	9.8E-09	0.0098
Cream	**Pb**	1.8E-05	18.492
Face Powder	**Pb**	1.1E-05	10.677
Eye Pencil	**Pb**	6.2E-10	0.0006
Eye shadow	**Pb**	1.3E-08	0.0126

CONCLUSION

Heavy metal contents within the studied cosmetics were ordered as Fe>Pb>Mn>Zn>Cr>Ni>Cu>Cd and Hg at all cosmetics. Where the dominant elements in PCPs were Fe, Pb, Mn, Cr, Ni, Zn and Cu and the minimum concentrations were noted for Cd and Hg. The present study revealed that Pb were present in these brands of facial cosmetic products at concentrations above their specified limits by the Canadian authority, FDA, Italy and Germany while Ni, Cr were above the suggested technically avoidable limits. Systemic exposure dosage of heavy metals in PCPs in this study is less than the recommended daily intake, the estimated margin of safety for metals in these facial cosmetic products was greater than the proposed value of 100 set by the WHO. Eye pencils have highest MoS values compared with other facial cosmetic products investigated. The MoS values indicate that there is no risk associated with the concentrations of metals in these products. HQ value was lower than 1 indicated that the overall risks in both exposure pathways are within safe level. HI values were lower than 1 except in eye pencil indicating that there was no risk in using these samples. The maximum value of oral cancer risk was in cream and the minimum value was in eye pencils. In addition to the maximum value of cancer risk index 18.49 chances per million was observed in creams. The study emphasizes the urgent needs for strict national regulations for manufacturing of personal care products.

REFERENCES

[1]. Ullah H, Noreen S, Fozia M, Rehman A, Waseem A, Zubair S, Adnan M, Ahmad I. Comparative study of heavy metals content in cosmetic products of different countries marketed in Khyber Pakhtunkhwa, Paskistan. Arab J Chem 2013; 10 (1): 10-18. http://dx.doi.org/10.1016/j.arabjc.2013.09.021.
[2]. Gondal MA, Seddigi ZS, Nasr MM, Gondal B. Spectroscopic detection of health hazardous contaminants in lipstick using laser induced breakdown spectroscopy. J Hazard Mater 2010; 175 (1–3): 726–732.
[3]. Al-Saleh I, Al-Enazi S. Trace metals in lipsticks. Toxicol Environ Chem 2011; 93(6): 1149–1165.
[4]. Nnorom IC, Igwe JC, Oji-Nnorom CG. Trace metal contents of facial(make-up) cosmetics commonly used in Nigeria. Afr J Biotechnol 2005; 4(10): 1133–1138.
[5]. US FDA. United State Food Drug and Cosmetic Act on Hazardous Chemicals in Cosmetics. US FDA; 2011.
[6]. Abdel AF, Pingitor NE. Low levels of toxic elements in dead sea black mud and smut derived cosmetic products. Environ Geochem Health 2009; 31(4): 487–492.
[7]. IPCS, International Programme on Chemical Safety. Dermal Exposure. Environmental Health Criteria. IPCS 2014; Vol. 242, WHO.
[8]. Ikarashi Y, Momma J, Tsuchiya T, Nakamura A. Evaluation of skin sensitization potential of nickel, chromium, titanium and zirconium salts using guinea-pigs and mice. Biomoterials 1996; 17: 2103–2106.
[9]. Sainio E, Jolanki R, Hakala E, Kanerva L. Metals and arsenic in eye shadows. Contact Dermatitis 2000; 42: 5–10.
[10]. Bergback B, Anderberg S, Lohm U. Lead load: Historic pattern of lead use in Sweden. Ambio 1992; 21 (2): 159–165.
[11]. Koller K, Brown T, Spurgeon A, Levy L. Recent developments in low level lead exposure and intellectual impairment in children. Environ Health Perspect 2004; 112(9): 987–994.
[12]. Adebajo D. An epidemiological survey of the use of cosmetic skin lightening cosmetics among traders in Lagos, Nigeria. West Afr J Med 2002; 1: 51-55.
[13]. Lavilla I, Cabaleiro N, Costas M, de la Calle I, Bendicho C. Ultrasound assisted emulsification of cosmetic samples prior to elemental analysis by different atomic spectrometric techniques. Talanta 2009; 80: 109–116.
[14]. HC-SC, Health Canada-Santé Canada. Cadmium and its compounds. HC-SC; 1994. Available at: <http://www.hc-sc.gc.ca/ewh-semt/pubs/contaminants/psl1-lsp1 cadmium comp/index-eng.php>. [Accessed 14 October 2013].
[15]. C-SC, Health Canada-Santé Canada. Arsenic and its compounds. HC-SC; 1993. Available at: <http://www.hc-sc.gc.ca/ewh-semt/pubs/contaminants/psl1-lsp1/ arsenic_comp/index-eng.php>. [Accessed 14 October 2013].
[16]. IARC, International Agency for Research on Cancer. Beryllium, Cadmium, Mercury, and Exposures in the Glass Manufacturing Industry. Vol. 58. IARC, Lyon, France, 1993.

[17]. IARC, International Agency for Research on Cancer. Arsenic, metals, fibres, and dusts. Vol. 100 C, IARC, Lyon, France, 2012.
[18]. Iwegbue CMA, Bassey FI, Obid G, Tesi GO, Martincigh BS (2016.(Concentrations and exposure risks of some metals in facial cosmetics in Nigeria. Toxicology Reports 2016; 3: 464–472.
[19]. Omenka SS and Adeyi AA. Heavy metal content of selected personal care products (PCPs) available in Ibadan, Nigeria and their toxic effects. Toxicology Reports 2016; 3: 628–635.
[20]. Volpe MG, Nazzaro N, Coppola R, Rapuano F, Aquino RP. Determination and assessment of selected heavy metals in eye shadow cosmetics from China, Italy and USA. Microchem J 2012; 101: 65–69.
[21]. Zhang C, Guo S, Huang C. Determination of compositions in cosmetics by multiple-instrument. Am J Anal Chem 2011; 2: 857–862.
[22]. Al-Dayel O, Hefne J, Al-Ajyan T. Human exposure to heavy metal from cosmetics, Orient. J Chem 2011; 27(21): 1–11.
[23]. Al-Qutob MA, Alatrash HM, Abol-Ola S. Determination of different heavy metals concentrations in cosmetics purchased from Palestinian markets byICP/MS, Adv. Environ. Sci Bioflux 2013; 5(3): 287–293.
[24]. Sani A, Gaya MB, Abubakar FA (2016). Determination of some heavy metals in selected cosmetic products sold in kano metropolis, Nigeria. Toxicology Reports 2016; (3): 866–869.
[25]. Murphy T, Slotton DG, Irvine K, Sukontason K, Goldman CR. Mercury contamination of skin whiteners in Cambodia. Hum Ecol Risk Assess 2009; 15: 12086–12103.
[26]. El-Shazly EAA, Abo Zahra SF, El-Sweify FH, Kanias GD. Simultaneous multi-element determination in some cosmetic samples of different origins using neutron activation analysis. Radiochim Acta 2004; 92: 111–117.
[27]. Al-Saleh I, Al-Enazi S, Shinwari N. Assessment of lead in cosmetic products. Regul Toxicol Pharm 2009; 54: 105–113.
[28]. ED, Environmental Defense Canada. Heavy Metal Hazard. The Health Risks of Hidden Heavy Metals in Face Makeup. Environmental Defense, Toronto, Canada, 2011(accessed 10.10.13) http://environmentaldefence.ca/sites/default/files/report files/HeavyMetalHazard %20FINAL.pdf.
[29]. Al-Ashban RM, Aslam M, Shan H. Kohl (Surna): A toxic traditional eye cosmetics study in Saudi Arabia. Public Health 2004; 114(4): 292–298.
[30]. US EPA (United States Environmental Protection Agency), Regional Screening Level Table (RSL) for Chemical Contaminants at Superfund Sites, U.S. Environmental Protection Agency, Washington, DC, USA, 2011.
[31]. AOAC. Official Methods of Analysis of AOAC INTERNATIONAL. OMA print; 20th Edition, AOAC; 2016.
[32]. SCCS, Scientific Committee on Consumer Safety. The SCCS's Notes of Guidance for Testing of Cosmetic Substances and Their Safety Evaluation(SCCS/1501/12), 8th edition, Scientific Committee on Consumer Safety, SCCS, 2012 (The SCCS adopted this opinion at the 17th plenary meeting of 11 December, 2012).
[33]. Godt J, Scheidig F, Grosse-Siestrup C, Esche V, Brandenburg P, Reich A, Gronenberg DA. The toxicity of cadmium and resulting hazards for human health. J Occup Med Toxicol 2006; 1: 1–6.
[34]. Basketter DA, Angelini G, Ingbe RA, Kern PS, Merine T. Nickel, cadmium and cobalt in consumer products: revisiting safe levels in new millennium. Contact Dermatitis 2003; 49: 1–7.
[35]. Adepoju-Bello AA, Oguntibeju OO, Adebisi RA, Okpala N, Coker HAB. Evaluation of the concentration of toxic metals in cosmetic products in Nigeria. Afri J Biotechnol 2012; 97(11): 16360-16364.
[36]. Hutson DH, Dean BJ, Brooks TM, Hudson-Walker G. Genetic toxicology testing of 41 industrial chemicals. Research 1999; 153: 57–77.
[37]. Sah RC. Poisonous cosmetics, the problem of mercury in skin whitening creams in Nepal, VI+10. Kathmandu, CEPHED, 2012.
[38]. Liu S, Hammond SK, Rojas-Cheatham A. Concentrations and potential health risks of metals in lip products. Environ Health Persp 2013; 121(6): 705–710.