



King Saud University
Arabian Journal of Chemistry

www.ksu.edu.sa
www.sciencedirect.com



ORIGINAL ARTICLE

Comparative study of heavy metals content in cosmetic products of different countries marketed in Khyber Pakhtunkhwa, Pakistan



Hussain Ullah ^{a,b,*}, Shamsa Noreen ^a, Fozia ^c, Ali Rehman ^a, Amir Waseem ^b, Shumaila Zubair ^b, Muhammad Adnan ^a, Ijaz Ahmad ^{a,*}

^a Department of Chemistry, Kohat University of Science & Technology (KUST), Kohat-26000, Khyber Pakhtunkhwa, Pakistan

^b Department of Chemistry, Quid-i-Azam University, Islamabad 45320, Pakistan

^c KMU Institute of Medical Sciences, Khyber Medical University Peshawar, Kohat-26000, Khyber Pakhtunkhwa, Pakistan

Received 24 February 2013; accepted 11 September 2013

Available online 20 September 2013

KEYWORDS

Cosmetics;
Heavy metals;
Atomic absorption
spectrophotometer

Abstract The study was undertaken in order to determine heavy metal content in fifteen ($n = 15$) cosmetics products both imported and locally manufactured by unauthorized company marketed at district Kohat, Khyber Pakhtunkhwa, Pakistan. An analytical test was performed for eight metals in cosmetics products using flame atomic absorption spectrophotometer. The overall mean ($n = 15$) concentration for each heavy metal was analyzed i.e. Pb, Cd, Cu, Co, Fe, Cr, Ni, Zn were 141.6 ± 0.016 , 0.238 ± 0.001 , 26.62 ± 0.012 , 0.527 ± 0.002 , 860.8 ± 0.061 , 0.074 ± 0.002 , 0.674 ± 0.002 and 268.6 ± 0.086 $\mu\text{g/g}$, respectively. The results of our study revealed that the concentrations of Fe, Zn, Pb and Cu in the samples within each class under investigation were higher. It also emphasize that the spurious nature of these products cannot be ignored because most of the developing and under developed countries are facing the problems to manufacture good cosmetics products. Hence, are selling these products under the brand name of well reputed national and international companies. Since no safe limit relating to cosmetic products is available in Pakistan, it is therefore difficult to ascertain if the values of metals obtained in this study are too high or low. Prolonged use of such products containing these elements may pose threat to human health and could curb the beauty of the environment.

© 2013 Production and hosting by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

* Corresponding author. Tel.: +92 927308219.

E-mail addresses: chem.hussain@gmail.com (H. Ullah),
drijaz_chem@yahoo.com (I. Ahmad).

Peer review under responsibility of King Saud University.



Production and hosting by Elsevier

1. Introduction

Cosmetics products since the dawn of civilization (Brown, 2013) are considered a part of routine body care. During the last few decades these products have had a big boost (Al-Dayel et al., 2011) and applied to the human body for beautification. These cosmetic products include, care creams, talcum and face

<http://dx.doi.org/10.1016/j.arabjc.2013.09.021>

1878-5352 © 2013 Production and hosting by Elsevier B.V. on behalf of King Saud University.

This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Table 1 Descriptive statistical summary of heavy metal concentration (mean \pm SD) in different cosmetic products in $\mu\text{g/g}$ (ND = not detectable).

Sample Code	Product name	Origin/market site	Color	Pb	Cd	Cu	Co	Fe	Cr	Ni	Zn
<i>Lipsticks</i>											
L-1	Ponds detox	Tokyo-Japan	Red	11.2 \pm 0.013	0.21 \pm 0.000	0.026 \pm 0.027	0.3 \pm 0.004	540 \pm 0.5	ND	0.795 \pm 0.002	0.790 \pm 0.011
L-2	ADS Lipstick	China	Pink	2.584 \pm 0.005	0.200 \pm 0.001	1.928 \pm 0.002	0.525 \pm 0.003	258 \pm 0.009	ND	0.696 \pm 0.001	0.437 \pm 0.017
L-3	Medora matte	Swat -Pakistan	Green Shiny	11.33 \pm 0.02	0.430 \pm 0.005	6.036 \pm 0.01	0.872 \pm 0.004	1164 \pm 0.15	0.774 \pm 0.019	1.610 \pm 0.009	5.99 \pm 0.01
Mean \pm SD (n = 3)				8.371 \pm 0.01	0.28 \pm 0.002	2.66 \pm 0.013	0.565 \pm 0.003	654 \pm 0.069	0.258 \pm 0.006	1.033 \pm 0.004	2.405 \pm 0.012
<i>Powder</i>											
P-1	Ponds dream flower	India (Hindustan) unilever Limit	White	2.325 \pm 0.002	0.258 \pm 0.001	1.095 \pm 0.002	0.66 \pm 0.002	1067 \pm 0.02	ND	0.72 \pm 0.002	1067 \pm 0.208
P-2	Ponds oil control talc	Hindustan (India) lever limited	Light Pink	3.105 \pm 0.002	0.36 \pm 0.001	1.515 \pm 0.004	1.02 \pm 0.002	652.0 \pm 0.01	ND	1.185 \pm 0.001	1.818 \pm 0.05
P-3	Ponds dream flower	Unilever Pakistan	White	3.975 \pm 0.006	0.325 \pm 0.000	1.362 \pm 0.003	1.225 \pm 0.005	779.8 \pm 0.011	0.262 \pm 0.006	1.425 \pm 0.003	649.8 \pm 0.078
Mean \pm SD (n = 3)				3.135 \pm 0.033	0.314 \pm 0.003	1.362 \pm 0.003	0.968 \pm 0.003	832.9 \pm 0.013	0.131 \pm 0.002	1.11 \pm 0.003	572.8 \pm 0.12
<i>Surma (Kohl)</i>											
S-1	Lidena eye liner	Unkown	Black	2.774 \pm 0.002	0.095 \pm 0.001	0.228 \pm 0.007	0.342 \pm 0.001	116.9 \pm 0.09	ND	0.290 \pm 0.003	1.362 \pm 0.02
S-2	Latif surma	Pakistan	Black	1071 \pm 0.060	0.942 \pm 0.006	302.2 \pm 0.008	0.72 \pm 0.003	1272 \pm 0.05	0.078 \pm 0.007	1.014 \pm 0.001	508.8 \pm 0.064
S-3	Hashmi Surma	Unknown	Black	1005 \pm 0.005	0.229 \pm 0.001	11.31 \pm 0.006	0.621 \pm 0.002	281.7 \pm 0.015	ND	0.702 \pm 0.001	253.5 \pm 0.015
Mean \pm SD (n = 3)				692.9 \pm 0.022	0.422 \pm 0.002	104.57 \pm 0.007	0.561 \pm 0.002	556.86 \pm 0.051	0.026 \pm 0.002	0.668 \pm 0.001	254.55 \pm 0.033
<i>Cream</i>											
C-1	Fair and lovely	Dubai	White	3.708 \pm 0.058	0.041 \pm 0.001	2.9 \pm 0.002	0.233 \pm 0.003	2250 \pm 0.034	ND	0.258 \pm 0.002	0.646 \pm 0.021
C-2	Fair & lovely	India	Transparent	1.841 \pm 0.005	0.041 \pm 0.001	2.058 \pm 0.006	0.25 \pm 0.002	1846 \pm 0.060	ND	0.266 \pm 0.002	1.772 \pm 0.033
C-3	Fair & lovely	Unilever Pakistan Limited	White	1.741 \pm 0.004	0.058 \pm 0.000	65.34 \pm 0.010	0.225 \pm 0.001	2469 \pm 0.202	ND	0.308 \pm 0.001	32.83 \pm 0.017
Mean \pm SD (n = 3)				2.43 \pm 0.022	0.046 \pm 0.000	23.43 \pm 0.036	0.236 \pm 0.002	2188 \pm 0.096	ND	0.277 \pm 0.001	11.74 \pm 0.023

Table 1 (continued)

Sample Code	Product name	Origin/market site	Color	Pb	Cd	Cu	Co	Fe	Cr	Ni	Zn
<i>Shampoo</i>											
Sh-1	Head and shoulder	Dammam	Light Green	3.322 ± 0.046	0.058 ± 0.000	0.071 ± 0.003	0.183 ± 0.001	27.97 ± 0.139	ND	0.095 ± 0.002	0.496 ± 0.004
Sh-2	Head and Shoulder	Dubai	Light green	1.782 ± 0.010	0.121 ± 0.000	0.896 ± 0.002	0.373 ± 0.002	34.66 ± 0.008	ND	0.364 ± 0.002	4.977 ± 0.031
Sh-3	head and Shoulder	Pakistan-Karachi	White	2.30 ± 0.012	0.203 ± 0.000	2.387 ± 0.004	0.367 ± 0.004	154.2 ± 0.074	ND	0.386 ± 0.001	1500 ± 0.02
Mean ± SD				2.468 ± 0.022	0.127 ± 0.000	1.118 ± 0.003	0.307 ± 0.002	72.27 ± 0.073	ND	0.281 ± 0.001	501.82 ± 0.018
(n = 3)											
Over all mean ± SD (n = 15)				141.8 ± 0.016	0.238 ± 0.001	26.62 ± 0.012	0.527 ± 0.002	860.8 ± 0.061	0.074 ± 0.002	0.674 ± 0.086	268.6
Over all min				1.741	0.041	0.026	0.183	27.97	ND	0.095	0.437 ± 0.086
Over all max				1071	0.942	302.2	1.225	2469	0.774	1.61	1500
Total no of samples				n = 15							

powders, lipsticks, kajal, sindoor, eye makeup, mouthwashes etc. (Chauhan et al., 2010). Apart from the demand of availability of cosmetic products in markets, the health awareness draws the attention of researcher and clinician (Nnorom et al., 2005) to find the adverse effects regarding heavy metal contamination (Saeed et al., 2010; Barakat, 2011).

Some cosmetics are benign; others can cause or are supposed to cause harmful effects such as cancer, allergic reaction, mutations, respiratory problems as well as development and reproductive problems (CDC, 2003). For instance, an increase level of cadmium has been reported to cause inhibition of DNA mismatches. Zinc has been reported to cause the same signs of illness as does lead, and can easily be mistakenly diagnosed as lead poisoning (Theresa et al., 2013). Heavy metal poisoning takes place in the form of various diseases when ingested or inhaled (Saeed et al., 2011) as shown in Table 3.

1.1. Hazardous chemicals in cosmetics

Cosmetics have often been considered by many dermatologists, more harmful than good (Groot et al., 1994). These contain more than 10,000 ingredients which are linked to many diseases like cancer, birth defects, developmental and reproductive harm. Knowing the toxicity the (US FDA) bans nine ingredients including coal tar colors, formaldehyde, glycol ethers, lead, mercury, parabens, phenylenediamine, phthalates in cosmetic products.

1.1.1. Heavy metals

Metals have been used as instruments of murder and were sprayed by the British in World War 1 (Adal and Tarabar, 2013). Generally heavy metals are those whose density is five times greater than the density of water (Al-Trabulsy et al., 2013; Glanze et al., 1996). These includes: antimony, arsenic, bismuth, cadmium, cerium, chromium, cobalt, copper, gallium, gold, iron, lead, manganese, mercury, nickel, platinum, silver, tellurium, thallium, tin, uranium, vanadium and zinc. Even the essential metals when present in higher concentration become toxic (Glanze et al., 1996).

1.1.2. Topical absorption and toxicity of heavy metals

The toxicity of metal and its cure is well documented (Palpandi and Kesavan, 2012) from early times (370 B. C. E.), when Hippocrates diagnosed abdominal colic in a man who became a victim of metal toxicity in metal extraction. After this diagnosis, study on toxic interaction of metals took its pace. The landmark inquiry into mechanism of action of heavy metals was the work by (Voegtlin et al., 1923). The skin absorption of the salts of heavy metals varies greatly with different physical parameters (Lilley et al., 1988). Exposure to metals may occur through the diet, from medications, from the environment (Adal and Tarabar, 2013) and the use of cosmetics. The use of underarm cosmetics has been investigated as possible cause of breast cancer. A biological basis for breast carcinogenesis may be due to the binding of various chemical constituents to DNA and to promote growth of the damaged cells (Darbre, 2003). It is due to this reason that Directive 76/768/EEC banned the use of heavy metals, Cd, Co, Cr, Ni, and Pb as impurities in the preparation of cosmetics (Bocca et al., 2007).

Dermal exposure is expected to be the most significant route because most of the cosmetics products are directly

Table 2 Comparative values ($\mu\text{g/g}$) for heavy metals in different cosmetic products from different countries with similar work reported in the literature (Origin refers to location where samples were prepared and market site refer to a place where samples were marketed).

Product name	Origin/market site	Pb	Cd	Cu	Co	Fe	Cr	Ni	Zn	Refs.
Lipstics	Tokyo-Japan, China, Swat-Pakistan	2.58–11.33	0.2–0.430	0.026–6.036	0.3–0.872	258–1164	ND-0.77	0.696–1.610	0.696–1.610	This study
Powder	Hindustan, Pakistan	2.325–3.975	0.258–0.36	1.095–1.515	0.66–1.225	652–1067	ND-0.262	0.72–1.425	1.818–1067	
Surma	Unkown, Pakistan, Unkown	2.774–1071	0.095–0.942	0.228–302.2	0.342–0.72	116.9–1272	ND-0.078	0.29–1.014	1.362–508.8	
Cream	Dubai, India, Pakistan	1.741–3.708	0.041–0.058	2.058–65.34	0.223–0.225	1846–2469	ND	0.258–0.308	0.646–32.83	
Shampoo	Dammam, Dubai, Pakistan	1.782–3.322	0.058–0.203	0.071–2.387	0.183–0.373	27.97–154.2	ND	0.095–0.386	0.496–1500	
Hair Pomades	Marked at Ghana	1.30–17.70	4.20–6.800	0.70–12.80	10.66–25.35	81.60–421.0	ND	1.300–72.00	1.60–89.5	Amartey et al. (2011)
Facial talcum powders	Marked at Nigeria	0.4–41	ND-8.1	–	ND-2.4	–	ND-2.7	–	–	Nnorom (2011)
Medicated soap	Marked at Nigeria	–	0.090–0.440 (0.252)	0.185–0.871 (0.596)	–	–	0.020–0.392 (0.274)	–	0.422–0.886 (0.682)	Ayenimo et al. (2010)
Non-medicated soap	-	–	ND–0.05 (0.024)	0.103–0.516 (0.264)	–	–	0.01–0.295 (0.118)	–	0.201–1.104 (0.540)	
Medicated cream	-	–	0.063–0.361 (0.215)	0.571–0.933 (0.745)	–	–	0.192–0.474 (0.383)	–	0.539–1.104 (0.793)	
Non-medicated cream	-	–	0.016–0.082 (0.038)	1.829–6.847 (3.740)	–	–	0.027–0.119 (0.064)	–	0.136–0.355 (0.249)	
Hair cream	-	–	0.279–0.781 (0.553)	0.525–0.810 (0.783)	–	–	0.013–0.426 (0.135)	–	0.531–0.811 (0.725)	
Eye Liners	-	66.4–213.6 (120.5)	0.3–1.8 (1.0)	–	–	78.0–325.2 (169.2)	33.5–43.1 (37.6)	78.0–325.2 (8.43)	72.0–128.5 (91.5)	Nnorom et al. (2005)
Eye pencils	-	66.0–187.1 (123.2)	0.5–1.1 (0.7)	–	–	17.0–288.3 (97.2)	25.8–64.3 (39.9)	4.9–21.5 (12.1)	36.3–198.7 (100.9)	
Lipstick	-	28.7–252.4 (87.3)	0.5–2.4 (0.9)	–	–	92.2–632.0 (256.1)	20.5–58.8 (30.4)	7.0–22.8 (13.3)	42.3–174.8 (88.0)	
Moisturing cream	Marked at Bulgaria	ND	ND-1.33	2.27–17.85	ND-1.00	–	–	5.09	–	Theresa et al. (2013)
Henna	Marked at Saudi Arabia	1.29–16.48	–	–	–	–	–	–	–	Al-Saleh-and Coate (1995)
Eye shadow, lipstick and powders	Marked at Bulgaria	ND-41.1	–	–	–	–	–	–	–	Tsankov et Al. (1982)
Eye shadows	-	< 20 $\mu\text{g/g}$	–	–	–	–	–	–	–	Sainio et al. (2000)
Kohl (surma)	Marked at Saudi Arabia	17.61–32.37	–	–	–	–	–	–	–	Al-Ashban et al. (2004)
Lipstics	China, Taiwan, Thailand, Germany, USA, Italy	0.27–3760.0	–	–	–	–	–	–	–	Al-Saleh et al. (2009)
Eye shadows	China, France, USA	0.42–58.70	–	–	–	–	–	–	–	
Eye shade	Marked at Saudi Arabia	4.41–11.9	ND-0.266	14.4–37.3	1.28–31.3	1000–3760	5.89–7000	6.01–46.8	38.6–2000	Al-Dayel et al. (2011)
Maskara	Marked at Saudi Arabia	ND-2.18	0.002–0.035	ND-1.04	1.73–20.4	1000–9500	1.44–17.1	5–31.4	ND-63.1	

Table 3 Recommended limits and toxicity for some metals.

Sample nature	Pb	Cd	Cu	Co	Fe	Cr	Ni	Zn	Refs.
Drinking water [*]	0.01	0.003	0.010	2.000	0.3	0.050	0.020	3	WHO (1996)
Medicinal Plants ^{**}	10 ^{###}	0.3 ^{###}	10 ^{###}	0.2–0.3 ^{###}	20 ^{###}	50–200 ^{###}	< 1 ^{**}	100 ^{**}	Rehman et al. (2013)
Daily dietary intake ^{***}	20–545	70	340–400 (child), 900 (adult)	–	**8–10	11–25 (child), 30–35 (adult)	35	3–8 ^{**}	Saeed et al. (2011)
##Cosmetics	10 20	3 5	–	–	–	–	–	–	Health Canada (2007) Al-dayl et al. (2011)
Toxicity	Damages the fetal brain, diseases of the kidneys, circulatory system, nervous system and autoimmunity	Kidney damages, renal disorder, human carcinogen	Liver damage, Wilson disease, insomnia	Carcinogen, lungs problem, vomiting and nausea, vision and heart ailments	vomiting, dizziness, nausea, anorexia, headache and weight loss ^{###}	Headache, diarrhea, nausea, vomiting, carcinogenic	Dermatitis, nausea, chronic asthma, coughing, human carcinogen	Depression, lethargy, neurological signs and increased thirst	Barakat (2011); Zakir et al. (2009)

^{*} Values are in mg/L.^{**} Values are in mg/day.^{***} DDI in µg/day.^{###} µg/g (ppm) = mg/kg = µg/g.^{###} WHO, 2005.

applied to the skin. Oral exposure can occur from wearing of cosmetics products containing heavy metal impurities around the mouth and also from hand to mouth contact (Sainio et al., 2002). The Heavy metal ions when come in contact with human body, get absorbed and form complexes with carboxylic acid (–COOH), amine (–NH₂), and thiol (–SH) of proteins resulting in malfunctioning or death of the cells and consequently lead to a variety of diseases. The treatment of metal intoxication is achieved by using a chelating agent (i.e. chelation therapy) that binds with the metal ions and the complexes are then eliminated from the body (Pachauri and Flora, 2010).

Information on the exposure to metal toxins through dermal contact is very scanty, and few data exist on the personal care products (Ayenimo et al., 2010). Complete understanding of the mechanisms of toxicity and knowledge on the mode of action is of practical importance. Detail description of the toxicity of heavy metals and their mode of action is beyond the scope of this article. However, the logical steps by which toxicity results are typically as follows: Delivery of toxicants > reaction of toxicants with target molecules > manifestation of dysfunction > counter reaction (repair)/failure of counter reaction (disrepair) > toxicity. Mode of action typically starts with the reaction of metals with target molecules and ends with toxic manifestations (Prasad and Shanker, 2008). The aim of this project was to ascertain the quality of various cosmetics products on the basis of heavy metal concentration. This research project will attract people to select human friendly products. It will also bring awareness among the people not to place in the market any cosmetic products which are spurious and liable to cause damage to human health when it is applied under normal conditions of use.

2. Materials and methods

2.1. Sample collection

Samples of commonly used personal care products (cosmetics) were purchased from local markets of District Kohat. At these shops one can buy personal care products imported from developed, developing countries as well as locally manufactured by unauthorized national companies where no or less quality control measures are applied. Besides lifestyle, living conditions and culture, these products are in common use. Therefore, there is a growing concern about the toxic effects of metals in human population. Keeping in view its daily use and its possible health consequences, we purchased 15 samples including non-medicated shampoo, talc powders, lipsticks, surma (Kajal or kohls), and cream. All the samples were

Table 4 The highest concentration of heavy metals among samples under investigation.

Element	Sample code	Type	Concentration in µg/g
Pb	S-2	Surma	1071
Cd	–	–	0.942
Cu	–	–	302.2
Co	P-3	Powder	1.225
Fe	C-3	Cream	2469
Cr	L-3	Lipsticks	0.774
Ni	–	–	1.610
Zn	Sh-3	Shampoo	1500

transferred to the laboratory for the estimation of heavy metal analysis.

2.2. Reagents and standards

Analytical grade nitric acid (65%, Sigma Aldrich) and perchloric acid (70–72%, Sigma Aldrich) were used for sample preparation. Calibration standards for each heavy metal were prepared each day from the certified standard stock solution (1000 ppm-manufactured under ISO 9001 Quality Assurance system-Perkin Elmer) in the range from 0.5 to 10 ppm. All the solutions were prepared in double distilled water. Dilution correction was applied for samples diluted or concentrated during analysis.

2.3. Sample preparation

All plastic and glassware were washed, rinsed many times with tap water and then soaked in 5% HNO₃ solution for a minimum of 24 h and were followed rinsing with deionized water before use. Solid samples were dried in an oven at 105 °C to constant weight and then stored in desiccators. About 3.5 g of each of the dried samples was weighed into a porcelain crucible and dry-ashed in a muffle furnace by stepwise increase of the temperature up to 550 °C for few hours. The ash samples were digested with a few ml of IM HNO₃, evaporated near to dryness on a hot plate (Ayenimo et al., 2010) in fuming hood, cooled and then filtered with whatmann no. 42 (Saeed et al., 2011), and were diluted up to the mark (100 ml) into a calibrated flask.

Samples such as cream and lotion which could not be conveniently processed by dry-ashing, were wet digested (Saeed et al., 2011) with a 4:1 mixture of nitric acid (65%) and perchloric acid (70–72%) on a hot plate in fuming hood near to dryness (Ayenimo et al., 2010) by slowly increasing the temperature for 2–3 h because oily compounds are exothermic and burns with flame. In case brown or black color appeared then again the same procedure was repeated by adding the mixture of concentrated acid by slow and continuous heating until the evolution of white fumes (marking the end of the digestion process) and near to dryness (Theresa et al., 2013). The solutions were allowed to cool and filtered into a calibrated flask (100 mL) by whatmann no. 42, and were diluted up to the mark.

2.4. Sample analysis

Precise determination of heavy metal content in cosmetic products is quite important because there is a narrow margin of

safety between adequate amount and overconsumption. To analyze heavy metals, there are various methods currently available including inductively coupled plasma mass spectrometer (ICP-MS) (Al-Dayel et al., 2011), inductively coupled plasma optical emission spectrometry (Liu et al., 2009), sector field inductively coupled plasma mass spectrometry (SF-ICP-MS) (Bocca et al., 2007), Plasma fission Spectrograph (Parry and Eaton, 1991) etc. But most frequently used analytical method for the analysis of heavy metal contamination in cosmetic products is Flame atomic absorption spectrophotometer (FAAS) (Amartei et al., 2011; Saeed et al., 2011).

Therefore, this study was carried out on a Flame Atomic spectrophotometer (Perkin Elmer 400) for lead, cadmium, copper, cobalt, iron, chromium, nickel and zinc. The instrument working condition and parameters for the determinations are shown in Table 5. The readings were rounded off suitably according to the value of standard deviation from measurements in triplicate.

2.5. Statistical analysis

Results of the research were analyzed for statistical significance by using statistical package software, version 9. Values in the text are shown in tabulated form as mean \pm SD with ND as not detectable. This research was performed in triplicate analysis.

3. Results and discussion

The number of selected cosmetics products was fifteen, three each for lipsticks, powder, surma, cream and shampoo. An analytical estimation test was performed for eight elements in the lipsticks, talc powder, surma (Kohls), cream and shampoo from Kohat market, Pakistan summarized in Table 1. The data presented in Table 1 showed a marked difference from the data reported worldwide in the literature (Table 2). Comparing the results within each class it is clear that Fe, Zn, Pb and Cu concentration in the samples under investigation are higher (Fig. 1).

The overall ($n = 15$) mean concentration of heavy metals analyzed were: 141.6 ± 0.016 $\mu\text{g/g}$ (range 1.74–1071 $\mu\text{g/g}$) with highest concentration in Surma (S-2) and lowest in creams (C-1) for Pb; 0.238 ± 0.001 $\mu\text{g/g}$ (0.41–0.942 $\mu\text{g/g}$) with the highest concentration in surma (S-2) and minimum in cream (C-1 and C-2) for Cd; 26.62 ± 0.012 $\mu\text{g/g}$ (0.02–302 $\mu\text{g/g}$) with the highest concentration observed in surma (S-2) followed by the lowest concentration in lipsticks (L-1) for Cu; 0.527 ± 0.002 $\mu\text{g/g}$ (0.183–1.225 $\mu\text{g/g}$) with maximum concen-

Table 5 Operating conditions of atomic absorption spectrophotometer.

Heavy metals	Flame type	Wavelength (nm)	Slit width (nm)	Cathode lamp current (mA)	Acetylene flow (L/min)	Air flow (L/min)	Energy
Pb	Air-acetylene	283.31	2.7/1.05	10	2.50	10	67
Cd	—	228.80	2.7/1.35	4	—	—	61
Cu	—	324.75	2.7/0.8	15	—	—	75
Co	—	240.73	1.8/1.35	30	—	—	72
Fe	—	248.33	1.8/1.35	30	—	—	65
Cr	—	375.9	2.7/0.8	25	—	—	92
Ni	—	232.0	1.8/1.35	25	—	—	60
Zn	—	213.86	2.7/1.8	15	—	—	53

tration value in powder (P-3) and minimum value in shampoo (Sh-1) for Co; $860.8 \pm 0.061 \mu\text{g/g}$ ($27.97\text{--}2469 \mu\text{g/g}$) with the highest concentration in cream (C-3) and lowest one in shampoo (Sh-1) for Fe; $0.074 \pm 0.002 \mu\text{g/g}$ ($\text{ND}\text{--}0.774 \mu\text{g/g}$) with the highest concentration in lipstics (L-3) followed by lower concentration: not detectable in (L-1, L-2, P-1, P-2, S-1, S-3, all cream samples) for Cr; $0.674 \pm 0.002 \mu\text{g/g}$ ($0.095\text{--}1.610 \mu\text{g/g}$), the maximum value was in lipstics (L-3) and minimum value in shampoo (Sh-1) for Ni; and $268.6 \pm 0.086 \mu\text{g/g}$ ($0.637\text{--}1500 \mu\text{g/g}$) with the highest concentration for Zn was analysed in Shampoo (Sh-3) sample.

Based on the mean concentrations (Table 2), the mean ($n = 3$) heavy metal contents were arranged in the following decreasing order: Fe > Pb > Cu > Zn > Ni > Co > Cd > Cr for lipstics; Fe > Zn > Pb > Cu > Ni > Co > Cd > Cr for powder; Pb > Fe > Zn > Cu > Ni > Co > Cd > Cr for surma (Kohl); Fe > Cu > Zn > Pb > Ni > Co > Cd > Cr for cream; Zn > Fe > Pb > Cu > Co > Ni > Cd for shampoo. Most of the cosmetic products in this study were found to contain high concentration of heavy metals, particularly, Pb, Cu, Fe and Zn which showed a wide variation among the samples (Fig. 1). The optimum values of heavy metals in different cosmetics products have also been displayed (Table 4), showing the importance of the results. There values of heavy metals in each class were nearly close to each other which made the results more interesting.

Keeping in view their toxicology, the estimation of toxic metals in cosmetic products has prompted us to carry out this study. Unfortunately there are no current international standards for impurities like heavy metals in cosmetics except 20 for lead and $5 \mu\text{g/g}$ for cadmium (Al-Dayel et al., 2011). The Canadian regularity limits for certain metals in cosmetics are 10 for Pb, 3 for As, Cd, Hg and $5 \mu\text{g/g}$ for Sb (Health Canada, 2011). Heavy metals are considered toxic above normal backgrounds as shown in Table 3. These limits are based to provide a high level of protection to susceptible consumer (Al-Dayel et al., 2011).

The comparison with literature (Table 2) of current study (Table 1) revealed that the concentrations of heavy metals in cosmetic products are: The highest concentration of Pb found

in surma ($1071 \mu\text{g/g}$) was lower than those obtained for mascara ($9500 \mu\text{g/g}$) (Al-Dayel et al., 2011); the highest concentration of Cd ($0.942 \mu\text{g/g}$) in surma was found to be lower than maximum value of hair pomade ($6.80 \mu\text{g/g}$) and higher than most of the investigations in the literature (Table 2); maximum concentration of Cu ($302 \mu\text{g/g}$) was found to be higher than all of the studies conducted for cosmetic products; the maximum value of Co ($1.02 \mu\text{g/g}$) obtained for powder in this study was found to be lower than those reported elsewhere (Nnorm, 2011); the value for Fe ($2468 \mu\text{g/g}$) for cream was found to be higher than cream and lower than eye shade (3760) reported in the literature (Al-Dayel et al., 2011); the highest concentration of Cr, Ni and Zn in our study was found to be lower than the reported value (Table 2). Various other studies have also been reported for heavy metal concentration in different cosmetic products (Al-Dayel et al., 2011). It is recommended that the consumer of cosmetics products must be selective while purchasing these products.

Knowledge about the prolonged use of cosmetic products and its subsequent health effects are lacking. We are a culture in love with lipstick which starts very early for many women. A recent survey conducted in 2004 showed most of the US girls aged 7–19 with 63 percent are using lipstics. When lips are licked, while eating and drinking, kissing someone wearing lipstics, we ingest the ingredient of lipstics. It is a common quote that “women inadvertently eat about 4 lb of lipstics in a lifetime”. A poison kiss which is associated with direct ingestion of lipstics containing lead may increase the level of lead in human body (CSC, 2007). The elevated level of lead found in two of the samples indicates that pregnant women are vulnerable population because it can easily pass through the placenta. Cadmium is known to be toxic in cosmetics like talcum powder and its toxicity increases in case of children. Studies of the health effects conducted on Kohl, a highly contaminated eye cosmetic product showed that adult absorb 5–15 and children can absorb round about 41% of the ingested lead (Al-Dayel et al., 2011). These heavy metals bind with the protein of the cell, thus hindering its function and causing death of the cells which lead to multiple diseases (Prasad and Shanker, 2008). The present study has only demonstrated that cosmetic

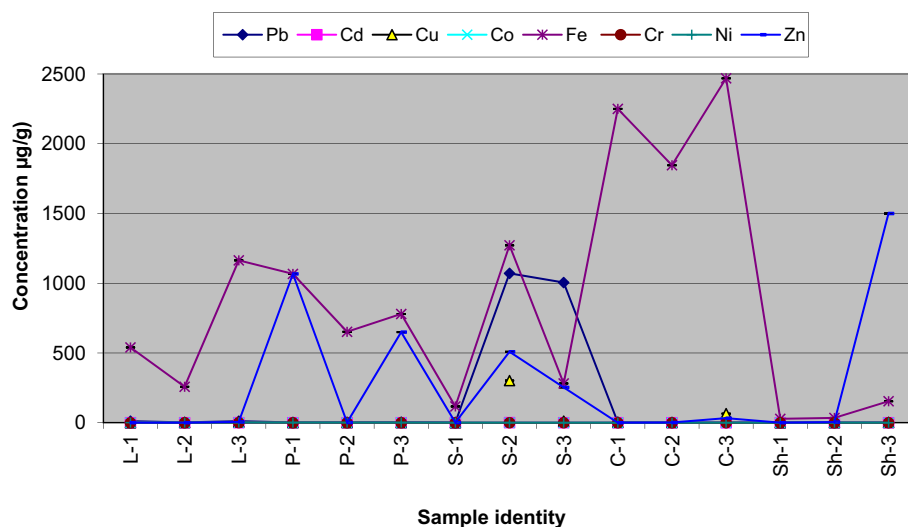


Figure 1 Comparative mean concentration of heavy metal content in cosmetic products.

products are notable sources of Pb, Cd, Cu, Co, Fe, Cr, Ni and Zn in human body as well as in the environment. Further study is required on the absorbed level and the number of persons exposed to it, particularly susceptible group and a highly exposed group. Therefore, there is a need for the establishment of regulations for heavy metals in personal care products as this will act to prevent harm in advance from the use of these products.

4. Conclusion

This study investigated the level of heavy metals in cosmetic products of different countries marketed in Khyber Pakhtunkhwa, Pakistan. It provided new data on heavy metal concentration in cosmetic products used in Pakistan. Only two samples contained high level of Pb concentration, four samples with high level of Zn, whereas most of these cosmetic products contained high level of Fe. For cosmetics i.e. lipsticks, talc powder, surma, cream and shampoo, dermal exposure is suspected to be the most significant exposure route since they are in direct contact with the skin.

It revealed that high and nearly close values of heavy metals among samples of each class may be due to the spurious nature (fake branded name) of the samples. It will be premature to jump at the conclusion to decide the fate of these products on the bases of concentration of heavy metals as there are no proper safety regulations in Pakistan. However, the possibilities of spuriousness of these products cannot be ignored. The data obtained clearly showed that further studies are also needed of these heavy metals in cosmetic products of daily use. Acceptable limits of potential contaminants in cosmetics must be enforced. The principle of good manufacturing practice must be followed. There is need for an assessment of human risk from the exposure to cosmetics which are highly contaminated with heavy metals. It was inferred from the result that most of the products were Pakistani (highly), Indian (fairly) and brands of some other countries (less) were contaminated with heavy metals. Removal of heavy metals from personal care products after manufacture is not possible, however if careful selection of the raw material is made keeping in view the heavy metal contents we can improve the quality of the products and save the beauty of the environment.

References

- Adal, A., Tarabar, A., 2013. Heavy Metal Toxicity, <http://emedicine.medscape.com/article/814960-overview>.
- Al-Ashban, R.M., Aslam, M., Shah, A.H., 2004. Kohl (surma): a toxic traditional eye cosmetic study in Saudi Arabia. *Public Health* 118, 292–298.
- Al-Dayel, O., Hefne, J., Al-Ajyan, T., 2011. Human exposure to heavy metals from cosmetics. *Orient. J. Chem.* 27 (1), 01–11.
- Al-Saleh, I.A., Coate, L., 1995. Lead exposure in Saudi Arabia from the use of traditional cosmetics and medical remedies. *Environ. Geochem. Health* 170 (1), 29–31.
- Al-Saleh, I., Al-Enazi, S., Shinwari, N., 2009. Assessment of lead in cosmetics products. *Regul. Toxicol. Pharm.* 54, 105–113.
- Al-Trabulsi, H.A.M., Khater, A.E.M., Habani, F.I., 2013. Heavy elements concentrations, physicochemical characteristics and natural radionuclides levels along the Saudi coastline of the Gulf of Aqaba. *Arab. J. Chem.* 6, 183–189.
- Amartey, E.O., Asumadu-Sakvi, A.B., Adjei, C.A., Quashie, F.K., Duodu, G.O., Bentil, N.O., 2011. Determination of heavy metals concentration in hair pomades on the Ghanaian market using atomic absorption spectrometry technique. *Br. J. Pharmacol. Toxicol.* 2 (4), 192–198.
- Ayenimo, J.G., Yusuf, A.M., Adekule, A.S., Makinde, O.W., 2010. Heavy metal exposure from personal care product. *Bull. Environ. Contam. Toxicol.* 84, 8–14.
- Barakat, M.A., 2011. New trends in removing heavy metals from industrial wastewater. *Arab. J. Chem.* 4, 361–377.
- Bocca, B., Forte, G., Petrucci, F., Cristaudo, 2007. A Levels of nickel and other potentially allergenic metals in Ni-tested commercial body creams. *J. Pharm. Biomed. Anal.* 44, 1197–1202.
- Brown, V.J., 2013. Metals in lip products: a cause for concern. *Environ. Health Perspect.* 121, 196.
- CDC, Centers for Disease Control and Prevention, 2003. Second National Report on Human Exposure to Environmental Chemicals. <http://www.cdc.gov/exposurereport/2nd/>.
- Chauhan, A.S., Bhadauria, R., Singh, A.K., Lodhi, S.S., Chaturvedi, D.K., Tomari, V.S., 2010. Determination of lead and cadmium in cosmetics products. *J. Chem. Pharm. Res.* 2 (6), 92–97.
- CSC, the Campaign for Safe Cosmetics, 2007. A poison kiss: the problem of lead in lipsticks. Available from: <<http://www.safe-cosmetics.org/about/reports.cfm>>.
- Darbre, P.D., 2003. Underarm cosmetic and breast cancer. *J. Appl. Toxicol.* 23 (2), 89–95.
- Glanze, W.D., Louis, S., Mosby, C.V., 1996. Mosby Medical Encyclopedia, Revised edition.
- Groot, A.C.D., Nater, J.P., Weyland, J.W., 1994. Unwanted Effects of Cosmetics and Drugs Used in Dermatology, third ed. (issue 1). Elsevier, pp. 2–15.
- Health Canada, 2007. Natural Health Products Directorate. Evidence For Quality Of Finished Natural Health Products.
- Health Canada, January 2011. Consumer product safety: Draft guidance on heavy metal impurities in cosmetics. <http://www.hcsc.gc.ca/cpspc/legislation/consultation/_cosmt/metalmtaux-consulteng.php>.
- Lilley, S.G., Florence, T.M., Stauber, J.L., 1988. The use of sweat to monitor lead absorption through the skin. *Sci. Total Environ.* 76 (267), 278.
- Liu, H., Chen, L.P., Ai, Y.W., Yang, X., Yu, Y.H., Zuo, Y.B., et al., 2009. Heavy metal contamination in soil alongside mountain railway in Sichuan China. *Environ. Monit. Assess.* 152, 25–33.
- Nnorom, I.C., 2011. Trace metals in cosmetics facial talcum powders marketed in Nigeria. *Toxicol. Environ. Chem.* 93 (5/6), 1135–1148.
- Nnorom, I.C., Igwe, J.C., Oji-Nnorom, C.G., 2005. Trace metal contents of facial (make-up) cosmetics commonly used in Nigeria. *Afr. J. Biotechnol.* 4 (10), 1133–1138.
- Pachauri, V., Flora, S.J.S., 2010. Chelation in Metal Intoxication. *Int. J. Environ. Res. Public Health.* 7 (7), 2745–2788.
- Palpandi, C., Kesavan, K., 2012. Heavy metal monitoring using Nerita crepidularia-mangrove mollusc from the Vellar estuary, Southeast coast of India. *Asian Pac. J. Trop. Biomed.*, S358–S367.
- Parry, C., Eaton, J., 1991. Kohl: a lead-hazardous eye makeup from the third world to the first world. *Environ. Health Perspect.* 94, 121–123.
- Prasad, M.N.V., Shanker, A.K., 2008. Mode of action and toxicity of trace elements. *Public Health Rep.* 38, 1882–1912, Chapter 21.
- Rehman, A., Ullah, H., Ahmad, R., Ahmad, I., 2013. Population based study of heavy metals in medicinal plant *Capparis deciduas*. *Int. J. Pharm. Pharm. Sci.* 4 (1), 108–113.
- Saeed, M., Muhammad, N., Khan, H., Khan, S.A., 2010. Analysis of toxic heavy metals in branded Pakistani herbal products. *J. Chem. Soc. Pak.* 32, 471–475.
- Saeed, M., Muhammad, N., Khan, H., 2011. Assessment of heavy metal content of branded Pakistani herbal products. *Trop. J. Pharm. Res.* 10 (4), 499–506.

- Sainio, E.L., Jolanki, R., Hakala, E., Kanerva, L., 2000. Metals and arsenic in eye shadows. *Contact Dermatitis*. 42 (1), 5–10.
- Theresa, O.C., Onebunne, O.C., Dorcas, W.A., Ajani, O.I., 2011. Potentially toxic metals exposure from body creams sold in Lagos, Nigeria. *Researcher* 3 (1), 30–37.
- Tsankov, I.U., Iordanova, I., Lolva, D., Uzunova, S., Dinova, S., 1982. Hygienic evaluation of the content of heavy metals (lead and copper) in cosmetic products. *Probl. Khig* 7, 127–136.
- US FDA, United State Food Drug & Cosmetic Act on Hazardous Chemicals in Cosmetics. Available at: <<http://www.fda.gov/opacom/laws/fdcact/fdctoc.htm>> .
- Voegtlin, C., Dyer, H.A., Leonard, C.S., 1923. On the mechanism of the action of arsenic upon protoplasm. *Public Health Rep.* 38, 1882–1912.
- WHO, World Health Organization, 1996. *Guidelines for Drinking Water Quality*. 2nd Ed. Geneva, Switzerland
- WHO, World Health Organization, 2005. *Quality Control Methods for Medicinal Plant Materials*; WHO Geneva Switzerland.
- Zakir, S.N., Ihsanullah, I., Shah, M.T., Iqbal, Z., 2009. Effects of time intervals on level of heavy metals in Surface and Ground waters in Peshawar in Peshawar basin. *J. Chem. Soc. Pak.* 31 (5), 757–771.