

Heavy Metals Concentration in Facial Cosmetics

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Abstract

Heavy metals impurities in cosmetic products are common due to their natural abundance. However, they should be kept to a minimum wherever technically feasible. Most people, specially females, use cosmetic and their ingredients on a daily basis. Although human external contact with a substance rarely results in its penetration through the skin and significant systemic exposure, cosmetics produce local (skin, eye) exposure and are used in the oral cavity, on the face, lips, eyes and mucosa. Therefore, human systemic exposure to their ingredients can rarely be completely excluded.

Because metals can induce unwanted side effects in humans, to establish their contents in body-care cosmetics is important for quality and health controls. In this work we have selected nine most expensive brands of facial cosmetics (Base jelly, Whitener, Sheen and Face powder) from the Saudi market. Twenty-eight elements were detected by using Inductively Coupled Plasma Mass Spectrometer (ICP-MS) and a flow injection mercury system (FIMS). The mean, maximum and minimum concentrations of each element are reported.

Keywords: Heavy elements; Cosmetics; Inductively coupled plasma-mass spectrometry (ICP-MS); Flow injection mercury system (FIMS)

Introduction

Women are mainly used different cosmetic products of body care as a basic daily product and they are not aware of the dangers of heavy metals that contained in cosmetics. Even if cosmetic products have a tiny proportion of heavy metals; which, they could not be ignored as cosmetics are worn for a long period [1]. Thirty-five metals are of concern because of potential occupational or residential exposure; 23 of these are heavy metals: antimony, arsenic, bismuth, cadmium, cerium, chromium, cobalt, copper, gallium, gold, iron, lead, manganese, mercury, nickel, platinum, silver, tellurium, thallium, tin, uranium, vanadium, and zinc [2]. Trace amounts of these elements are common in our environment and diet and are actually necessary for good health, but large amounts of any of them may cause acute or chronic toxicity (poisoning). Heavy metal toxicity can result in damaged or reduced mental and central nervous function, lower energy levels, and damage to blood composition, lungs, kidneys, liver, and other vital organs. Long-term exposure may result in slowly progressing physical, muscular, and neurological degenerative processes that mimic Alzheimer's or Parkinson's disease, muscular dystrophy, and multiple sclerosis. Allergies are not uncommon and repeated long-term contact with some metals or their compounds may even cause cancer [3].

Lipsticks are one of the most important cosmetic product that women are commonly used to look more attractive and be in a good looking; however, they paid a high price by exposure to different heavy metals, which lipsticks are contained [1]. In 2007, the Campaign for Safe Cosmetics tested for and found-lead in numerous top-selling lipsticks [4]. It stood to reason that lipstick may not be the only product that could contain lead and not list it on the label. After

reports revealed that several other countries such as Italy [5] Ireland [6] and Canada [7] found heavy metals in face paints.

Lead is harmful, particularly so to the developing brain and nervous system [6,8] Lead can cause kidney damage, has been linked to cardiovascular disease and can cause autoimmune disorders [9]. Lead mainly enters the body through ingestion or inhalation of lead-dust. Adults absorb about 11% while children absorb 30-75% of lead that reaches the digestive tract. Less than 1% of lead is known to be absorbed through the skin [10]. Lead poisoning is a global problem. It is one of the most important environmental diseases in children [11]. Pregnant women and children 6 years or younger absorb lead in the highest quantities. Even low levels of lead exposure are considered hazardous to pregnant women [12]. Lead exposure during the first trimester of pregnancy has been found to cause alterations in the developing retina, thus leading to possible defects in the visual system [13]. Lead poisoning has been linked to juvenile delinquency and behavioral problems. Young children are particularly susceptible to lead poisoning due to their normal hand-to-mouth activity and because of the high efficiency of lead absorption by their gastrointestinal tracts [14]. Chronic low-dose lead exposure was found to cause renal tubular injury in children [15], while in adults, it was associated with poorly controlled hypertension [16]. A blood lead level of 10 mg/dl is of concern [8]. Shaltout et al. [17] found 20 patients aged between 1 and 18 months suffering from lead encephalopathy in Kuwait. The blood levels in 19 children ranged between 60 and 257 mg/dl. Two of these patients died before starting treatment, and three children died during treatment. Among the children who recovered, four had neurological sequelae. The source of lead in 11 patients was confirmed to be kohl [17]. On another reference, a seven-month-old baby was found to have a blood lead level of 39 mg/dl due to use of kohl [18]. In the USA, kohl and 'kajal' from the Middle East were considered among the unapproved dyes in eye cosmetics that contained potentially harmful amounts of lead [19]. Similarly, certain

traditional digestive remedies also contain harmful levels of lead [18]. Zakaria and Ho [1] studied lipsticks marketed in Malaysia for their heavy metal contamination. They have found lead concentrations of 0.8-15 mg/kg. There is no internationally agreed limit on permissible lead contents of lipsticks; but Health Canada stipulates it should not exceed 10 ppm.

Little is known about lead poisoning in Saudi Arabia. Studies have suggested that kohl in Saudi Arabia might be a cause of lead toxicity, [20,21] but no detailed investigation has been undertaken. The Saudi Standards, Metrology and Quality Organization issue a standard for the rouge samples, number 1871 in 2001. In this standard the concentration of As (as As₂O₃), Pb and Hg is limited to 2 mg/Kg, 20 mg/Kg, 1 mg/Kg respectively.

A certain degree of sensitization was shown by the salts of platinum group elements, i.e., Pt, Pd, Rh, and Ir, because of their large use in dental devices, jewellery, and automotive catalysts [22-24]. Moreover, a synergic action between Pd and Ni, pertaining to the same periodic group, has been suggested as being the cause of cross-sensitization [22]. Both Cu and Mn are rare skin sensitizers; immune reactions due to Cu exposure from intrauterine devices or by handling euro coins have been described, whereas the use of prosthetic materials in dentistry has created a risk of sensitization for both Cu and Mn [25,26]. Considering toxic metals such as Cd and Hg little is known about their dermatological activities. Cases of allergic contact dermatitis (ACD) due to Cd exposure from cement dust emission [27] and ceramics material [28] and to Hg present as ammoniated mercury (HgNH₂Cl) in skin lightening creams have been reported [29]. One case of sensitization to V was found in an enameller employed in the ceramics industry [28]. Another important way of skin exposure to metals is the use of cosmetic products such as moisturizing creams, lipsticks, eye cosmetics, shampoos, cleansing milk, henna dye, etc. In these make-up product metals are present as impurities due to the particular sample formulation or the release from metallic devices used during their manufacture. In fact, the European Communities Directive 76/768/EEC and further revisions banned the use of Cd, Co, Cr, Ni, and Pb as metallic ions or salts in the preparation of cosmetic formulations [30]. Considering the prolonged contact time of cosmetic products with the skin the risk of ACD might be increased [31,32]. As a support to this, there are several studies evidencing the presence of Co, Cr, Ni, and Pb at levels of µg g⁻¹ in henna dye, eye shadows, and lip liners with frequent positive reactions to patch tests [31,33-36]. Some authors revealed the presence of Cd, Cr, Cu, Hg, Pb, and metal oxides in body or sunscreen creams [37-39]. If the cosmetic products are formulated as dry, this will minimize the risk of skin penetration of metal, whereas those based on fat-soluble substances (for example moisturizing creams) promote the percutaneous absorption much more. On the other hand, adverse reactions to metal-containing cosmetic products were mostly observed in patients with manifestation of pre-existing allergy to metals [40]. Patch tests revealed that a threshold limit equal to 5000 ng g⁻¹ or for a more protection equal to 1000 ng g⁻¹ for Ni, Co and Cr excluded the risk of elicitation in sensitized people [39,40]. Given these facts and the increased frequency of allergy to Ni, the challenge of the cosmetic industry was to manufacture products to be used by people pre-sensitized to Ni. For this reason, manufacturers made available on the market creams labelled with the phrase "Ni-tested" together with a declared Ni concentration of 100 ng g⁻¹, thus guaranteeing levels 50 times below the risk of causing allergy reactions [40].

There is increasing evidence that the chemical constituents of underarm and body-care cosmetics applied to the underarm and breast area may be involved in the rising incidence of breast cancer [41-43]. Aluminium salts, such as aluminium chlorohydrate (ACH), are the active ingredients of antiperspirant [44]. Their mode of action is thought to involve blockage of the sweat ducts which prevents the escape of sweat onto the body surface, probably through the formation of a physical plug at the top of the sweat duct, which is composed of a combination of precipitated salts and damaged cells [44-47].

Because metals can induce unwanted side effects in humans establishing their contents in body-care cosmetics products is important for quality and health controls. The European Community directives forbid cosmetic formulations containing more than 1% selenium sulfide while zinc pyrithione cannot exceed 0.5% and other zinc salts are limited to 1% [48]. In this work, we have selected nine brands, which are the most expensive of the facial cosmetics (Base jelly, Whitener, Sheen and Face powder) from the Saudi market. Twenty-eight elements were detected by using Inductively Coupled Plasma Mass Spectrometer (ICP-MS) and a flow injection mercury system (FIMS).

Materials and Methods

Sample preparation

An accurately weighed sample of (0.1-0.2 g) was transferred to a TEFLON digestion tube (120 mL) mixed with 7.0 mL of the acid mixture (HNO₃/HF/HCl, 4.5:2:0.5). The tube was sealed. The sample was digested in a microwave oven (Milestone ETHOS 1600) following a heating program shown in Table 1.

After cooling to ambient temperature, the tube was unsealed; the inside of the lid was rinsed with distilled and de-ionized water (DDW) and the mixture heated on a hotplate (120 °C) for 30 min. to evaporate residual HF and HCl. The resulting digest was filtered in a polypropylene flask using 1% HNO₃ and made up to 50 ml volume. For ICP-MS measurement the clear digest obtained were diluted 10 times incorporating 10 µg L⁻¹ solution of ¹⁰³Rh. In general, samples and standard reference materials (SRM) were prepared in a batch of six including a blank (HNO₃/HF/HCl) digest.

Step	1	2	3	4
Power/W	400	0	300	400
Time/min	15	2	10	15
Temp/°C	195	195	195	195

Table 1: Microwave heating program used for dissolution of the samples.

Chemicals and reagents

High purity water (DDW) (Specific resistivity 18 MW.cm⁻¹) obtained from an E-pure water purification system (Barnsted, USA) was used throughout the work. HNO₃, HF and HCl used for sample digestion were of Suprapure grade with certified impurity contents (Merck, Germany). A multi-element standard containing 27 elements were prepared from Perkin-Elmer single-element ICP standards (1000 or 10000 ppm). The Standard Reference Material (SRM), IAEA-SOIL-7 was purchased from the International Atomic Energy Agency, Vienna.

Instrumentation

A Perkin-Elmer Sciex ELAN 6100 inductively coupled plasma mass spectrometer (ICP-MS), equipped with a quadrupole mass filter, a cross-flow nebulizer and a Scott type spray chamber, was used for all measurements.

Quality assurance

To assess the analytical process and make a comparative analysis, Standard Reference Materials (Soil 7) from the International Atomic Energy Agency (IAEA), Vienna, Austria was used. The quantitative analysis result is shown in Table 2. The results are generally in good agreement with certified values of the reference materials.

Elements	Certified Values	Actual work	
	95% Confidence Interval in ppm	ppm	RSD
Li	15-42	39.1	3.07
B		28.3	5.4
Na	2300-2500	2090	0.96
Mg	11000-11800	11200	1.05
Al	44000-51000	47900	0.287
K	11300-12700	11500	0.878
Ca	157000-174000	155000	1.09
V	59-73	73.7	0.982
Cr	49-74	62.8	3.33
Mn		648	1.13
Fe	25200-26300	25100	0.623
Co	8.4-10.1	12.4	4.32
Ni	21-37	17.2	2.22
Cu	9.0-13	11.2	1.16
Zn	101-113	115	0.0825
As	12.5-14.2	14	2.23
Se	0.2-0.8	1.3	34.6
Rb	47-56	50.2	0.327
Sr	103-114	102	1.35
Mo	0.9-5.1	1.03	3.47
Ag		0.484	3.3
Cd	1.1-2.7	1.13	0.726
Ba	131-196	131	1.36
Pb	55-71	61.7	0.262
U	2.2-3.3	2.07	0.544
Sb	1.4-1.8	1.57	1.91
Sn		2.84	2.79

Table 2: Concentration of elements in Soil 7.

Hg analyses

A flow injection mercury system (FIMS) from Perkin Elmer FIMS-400 was used for determination of Hg in the samples.

The FIMS is a complicated technique depending up on synchronization of mechanical, chemical and optical operations. The system contains three major units namely the spectrophotometer coupled with the flow injection circuitry, the amalgamation unit and

the computer unit for automated control of the operation and measurements. The FIAS program was optimized and the program is saved as “Mercury 2” in the computer, Table 3. The FIMS pumps program is shown in Table 4.

Method name:	Type	Diameter	Time
	Mercury 2	Slit width:	0.7 nm
Technique:	FIAS-MHS	Read time:	15.0 s
Wavelength:	253.4 nm	Read Delay:	0.0 s
BOC time:	2.0 s	Signal type:	AA
Measurement:	Peak height	Calibration:	Linear, zero intercept

Table 3: FIMS program.

Step	Time	Pump 1 speed	Pump 2 speed	Valve position	Read	Heat	Cool	Argon
Pre-fill	8	100	40	Fill			X	X
Step 1	5	100	40	Fill		X		X
Step 2	25	100	40	Fill			X	X
Step 3	20	0	40	Inject			X	X
Step 4	20	0	40	Inject			X	X
Step 5	10	0	40	Fill			X	X
Step 6	20	0	40	Fill	X	X		
Step 7	10	0	40	Fill			X	X
Step 8	1	0	0	Fill				
Steps to Repeat: 1 to 4		Number of repeats: 0						

Table 4: FIMS pumps program.

The blank used in this process contained 2 v/v% H₂SO₄, 2 v/v% HNO₃ and approx. 1.0 mg L⁻¹ KMnO₄ in de-ionized water. All the measuring standard and sample solutions were stabilized in the same medium.

Results and Discussion

Heavy metals are found naturally in the environment. They exist in manufactured pigments and other raw materials in all industries including cosmetics. Some of these metals have been used as cosmetic

ingredients in the past. Examples include the preservative thimerosal (mercury), the progressive hair dye lead acetate and a number of tattoo pigments such as red cinnabar (mercuric sulfide) [49]. The concentration of twenty elements in ppb (µg/Kg) in the facial cosmetics (Base jelly, Whitener, Sheen and Face powder) of nine brands of facial cosmetics. In addition, the mean, the minimum and the maximum of elemental concentration are reported in Tables 5-8. Inductively Coupled Plasma Mass Spectrometer (ICP-MS) and a flow injection mercury system (FIMS) were used to obtain the results.

Elements	Base jelly						
	Mean of nine brands	Min	RSD	Samples	Max	RSD	Samples
Li	14875.5	29.2		C46	39900	0.57	C55
B	11080.0	BDL		C37, C46, C55, C63 and C71	17600	12.9	C26
Na	2941444.4	353000	1.59	C37	13000000	0.79	C1
Mg	2029900.0	35100	2.45	C46	9970000	0.61	C9
Al	3661444.4	333000	1.06	C71	10200000	0.61	C9

K	987422.2	57800	3.37	C1	4650000	0.69	C9
Ca	133399.6	BDL		C17, C37, C46 and C55	434000	2.29	C26
V	694.4	198	1.97	C26	1590	0.83	C9
Cr	3853.3	1150	4.85	C17	12800	1.89	C71
Mn	9200.0	3610	1.3	C37	13800	0.81	C26
Fe	8464444.4	1300000	1.54	C63	17300000	0.32	C1
Co	932.8	204	2.14	C63	2070	2.41	C71
Ni	7539.4	BDL		C9 and C55	26100	0.98	C71
Cu	21368.9	8020	2.06	C9	34700	0.55	C46
Zn	58855.6	21900	2.72	C9	101000	0.36	C46
As	387.1	82.1		C71	1240	1.78	C26
Se	225.2	37.2		C26	582	16	C46
Rb	6241.9	88.1	7.63	C46	35800	1.47	C9
Sr	4351.4	262	6.01	C46	13400	0.26	C37
Mo	310.6	90.1	2.25	C26	662	3.6	C71
Ag	141.3	13.1		C37	499	2.69	C71
Cd	12.0	1.99		C71	38.2	10.2	C46
Ba	101979.6	966	1.67	C1	884000	0.47	C9
Pb	2024.9	157	1.11	C26	12200	0.83	C71
U	240.5	26.1	4.53	C1	1510	1.8	C71
Sb	1023.7	52.6	10.5	C9	3560	0.87	C1
Sn	60700.0	12600	0.81	C17	394000	0.3	C46
Hg	0.9	BDL		C17 and C37	16.45	5.03	C55

(BDL=below detection limit).

Table 5: The concentration of elements on the Base jelly samples in ppb.

Elements	Whitener						
	Mean of four brands	Min	RSD	Samples	Max	RSD	Samples
Li	14491.9	67.4		C36	29000	1.43	C45
B		BDL		C36, C45, C53	9550000	0.68	C25
Na	2405500.0	352000	1.14	C53	6150000	0.34	C45
Mg	934325.0	46300	3.67	C36	3200000	1.54	C45
Al	3196325.0	75300	1.22	C36	8010000	0.44	C25
K	1260250.0	138000	0.88	C36	4260000	0.95	C25
Ca	233650.0	BDL		C36 and C53	454000	2.99	C25
V	576.4	87.4	4.90	C36	1540	1.56	C25

Cr	1670.0	1040	6.08	C36	2290	0.51	C45
Mn	2250.5	115	8.11	C36	5790	1.32	C25
Fe	218925.0	22600	5.31	C36	613000	0.86	C25
Co	111.0	53.7	2.80	C53	204	2.70	C45
Ni	2897.0	BDL		C53	12500	1.37	C45
Cu	7466.7	BDL		C36	13600	2.83	C53
Zn	17425.0	1900	5.48	C36	42600	1.64	C53
As	236.0	97	13.20	C53	544	1.85	C45
Se	308.5	55		C36	1020		C45
Rb	7740.1	90.5	4.11	C36	25100	0.64	C25
Sr	1546.7	BDL		C36	2050	0.74	C45
Mo	275.5	124	8.41	C25	663	2.18	C45
Ag	33.7	13.7	15.50	C36	64.1	3.59	C53
Cd	30.8	12.4	18.70	C25	68.5	16.30	C45
Ba	5093.5	374	7.53	C36	12300	0.75	C25
Pb	557.8	104	0.30	C36	954	1.28	C25
U	283.4	92.5	4.39	C53	833	1.99	C45
Sb	98.1	BDL		C36	173	5.06	C45
Sn	20250.0	16500	0.43	C36	27900	0.68	C25
Hg	0.3	0.04	8.10	C36	0.61	1.80	C53

(BDL=below detection limit).

Table 6: The concentration of elements on the whitener samples in ppb.

Elements	Sheen						
	Mean of nine brands	Min	RSD	Samples	Max	RSD	Samples
Li	31287.9	931	8.21	C33	162000	1.83	C51
B	11995.7	BDL		C42 and C60	24700	3.88	C22
Na	421888.9	216000	1.71	C33	875000	1.97	C22
Mg	594966.7	30700	3.57	C42	2770000	0.23	C51
Al	4935555.6	1760000	0.90	C42	9860000	1.06	C22
K	1936666.7	408000	1.48	C33	4630000	1.27	C22
Ca	6895375.0	BDL		C6, C14, C22 and C76	27300000	0.68	C33
V	1215.6	208	3.22	C42	4180	1.15	C14
Cr	1927.8	1020	7.17	C68	3490	2.30	C14
Mn	7156.7	1080	1.68	C42	21500	0.84	C14
Fe	2075888.9	311000	1.57	C51	9280000	1.19	C14

Co	247.4	63.9	5.92	C68	810	10.60	C33
Ni	1456.2	BDL		C14, C22,51 and 60	2590	1.28	C76
Cu	21494.4	510	5.62	C42	177000	0.76	C33
Zn	59371.7	BDL		C6, C14 and C42	163000	0.21	C60
As	219.1	BDL		C76	853	4.28	C33
Se	142.3	BDL		C14, C22, C51 and C68	224	20.30	C60
Rb	15096.7	3690	0.46	C33	33700	0.69	C22
Sr	8483.0	55.7	8.72	C42	52900	0.60	C33
Mo	168.9	BDL		C68 and C76	228	5.05	C33
Ag	35.4	BDL		C22, C42 and C51	76	4.15	C33
Cd	8.9	BDL		C14, C68 and C76	19.8	12.50	C33
Ba	534331.1	3870	1.99	C42	4240000	0.84	C33
Pb	3114.2	190	1.22	C42	22500	0.29	C33
U	95.7	BDL		C68	288	1.29	C33
Sb	39.7	4.1	67.20	C6	107	2.87	C33
Sn	26911.1	17200	1.64	C68	46800	1.26	C33
Hg	12.6	BDL		C6, C14 and C22	52.1		C51

(BDL=below detection limit).

Table 7: The concentration of elements on the Sheen samples in ppb.

Elements	Face Powder						
	Mean of eight brands	Min	RSD	Samples	Max	RSD	Samples
Li	17995.9	161	1.36	C78	63700	0.78	C62
B	1345945.9	BDL		C35, 70 and 78	10700000	1.51	C24
Na	944625.0	289000	1.52	C35	2570000	0.40	C24
Mg	13602500.0	4070000	0.43	C78	26300000	1.04	C44
Al	10111500.0	374000	0.35	C78	31000000	0.59	C24
K	10165637.5	15100	4.20	C8	29100000	1.07	C24
Ca	2768625.0	420000	3.16	C24	11600000	0.57	C62
V	5216.3	1420	2.01	C70	15700	0.77	C24
Cr	3400.0	1780	2.02	C16	5510	1.19	C35
Mn	46725.0	22200	1.07	C8	117000	0.46	C24
Fe	4391250.0	1210000	1.52	C78	8780000	0.42	C70
Co	2248.9	488	2.23	C70	5350	1.38	C35
Ni	6557.7	41.4		C24	22300	1.90	C35
Cu	6829.5	BDL		C24	20300	1.44	C70

Zn	5429993.8	2120	3.31	C16	24400000	0.83	C70
As	441.9	156	11.70	C8	793	6.62	C35
Se	1483.8	514	15.80	C8	4450	13.40	C44
Rb	53434.9	399	5.46	C8	185000	0.57	C62
Sr	5108.3	622	1.46	C70	24400	0.38	C24
Mo	382.8	BDL		C70	1210	2.97	C35
Ag	283.6	31.4	11.50	C62	1600	2.13	C24
Cd	47.1	4.63		C16	155	12.40	C24
Ba	41846.3	2220	1.22	C70	157000	1.06	C24
Pb	4194.3	934	2.33	C8	7710	0.73	C62
U	1789.8	91.2	2.13	C70	3250	1.07	C35
Sb	774.4	71	16.40	C16	2650	0.81	C24
Sn	31337.5	17900	0.28	C16	65100	0.31	C44
Hg	2.8	BDL		C8, C16, C24, C35, C44 and C78	5.2	0.98	C62

(BDL=below detection limit).

Table 8: The concentration of elements on the Face Powder samples in ppb.

When compared to the mean concentration of elements in the facial cosmetics samples (base jelly, whitener, sheen and face powder) under investigation, we observed:

The mean concentration of elements in whitener samples were the lowest among the fifteen elements (Li, B, Al, V, Cr, Mn, Fe, Co, Zn, Sr, Ag, Ba, Pb, Sn and Hg). In this work whitener samples do not record any element with highest mean concentration. Face powder samples record the highest mean concentration of the sixteen elements (B, Mg, Al, K, V, Mn, Co, Zn, As, Se, Rb, Mo, Ag, Cd, Pb and U). Only one element, copper, in face powder samples showed the lowest mean concentration. Base jelly samples had three elements with the lowest mean concentration (K, Ca and Rb) and six elements with the highest mean concentration (Na, Cr, Fe, Ni, Sb and Sn). Sheen samples had nine elements with the lowest mean concentration (Na, Mg, Ni, As, Se, Mo, Cd, U and Sb) and six elements with the highest mean concentration (Li, Ca, Cu, Sr, Ba, Hg).

Conclusion

It is acknowledged that heavy metal impurities in cosmetic products are unavoidable due to the ubiquitous nature of these elements, but should be removed wherever technically feasible.

Cosmetic in general can have a high concentration of trace-metal elements. Given the significant and relatively uncontrolled human exposure to cosmetics and their ingredients, these products must be thoroughly evaluated for their safety prior to marketing [50-54].

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