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## Human Exposure to Heavy Metals from Cosmetics

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### ABSTRACT

Heavy metal impurities in cosmetic products are unavoidable due to the ubiquitous nature of these elements, but should be removed wherever technically feasible. Most of 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, cosmetic 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. Given the significant and relatively uncontrolled human exposure to cosmetic and their ingredients, these products must be thoroughly evaluated for their safety prior to their marketing. In this work we chose nine brands of the most expensive brands names of Mascara and Eye Shade from the Saudi market. Twenty eight elements were determined by using Inductively Coupled Plasma Mass Spectrometer (ICP-MS) and a flow injection mercury system (FIMS).

**Key words:** Cosmetics, Mascara, Eye Shade, Heavy Metal.

### INTRODUCTION

During the past decades the safety of cosmetic products and their ingredients has attracted increasing attention; thus their toxicological safety evaluation is a relatively young discipline, which evolved in the second half of the 20th century. Up to the 1960s it was generally believed that cosmetic products will always remain on the surface of the human body. Therefore, local effects were the primary safety concern. The first standardized in vivo tests for skin and eye irritation were developed in the 1940s by Draize (1944)<sup>1</sup>. Additional tools for the safety evaluation of cosmetic products,

such as in vivo sensitization-, phototoxicity-, photosensitization- animal and clinical safety tests, were developed in the 1960s and 1970s. During the past decades it was recognized that some topically applied substances may penetrate into or through human skin and produce human systemic exposure; this prompted the development of tests on the percutaneous penetration potential of cosmetic products ingredients as well as investigation of their potential systemic toxicity<sup>2</sup>. Finally, during recent years, new alternative test methods were developed and are increasingly being applied to the safety assessment of cosmetic products and their ingredients; these methods may

replace animal tests within the forthcoming years assuming their proper development, validation, and scientific understanding<sup>3</sup>.

Lead is harmful to all adults, children and infants. It is particularly harmful to the developing brain and nervous system<sup>4</sup>. Lead mainly enters the body through oral ingestion or inhalation of lead dust. Adults absorb about 11% and children absorb 30–75% of lead that reaches the digestive tract. Less than 1% of lead is known to be absorbed through the skin<sup>5</sup>. Lead poisoning is a global problem, considered to be the most important environmental disease in children<sup>6</sup>. Pregnant women and children under 6 years of age absorb lead in the highest quantities, and even low levels of lead exposure are considered hazardous to pregnant women<sup>7</sup>. 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 in future<sup>8</sup>.

Lead poisoning has been linked to juvenile delinquency and behavioural 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<sup>9</sup>. Chronic low-dose lead exposure was found to cause renal tubular injury in children<sup>10</sup>, while in adults, it was associated with poorly controlled hypertension<sup>11</sup>. A blood lead level of 10 mg/dl is of concern<sup>4</sup>. Shaltout *et al.*<sup>12</sup> 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<sup>12</sup>.

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<sup>13</sup>. 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<sup>14</sup>. Similarly, certain traditional digestive remedies

also contain harmful levels of lead<sup>13</sup>. Little is known about lead poisoning in Saudi Arabia. Studies have suggested that kohl in Saudi Arabia might be a cause of lead toxicity,<sup>15,16</sup> but no detailed investigation has been undertaken.

In addition to lead, as a non-essential element, aluminium might also be toxic at both environmental and therapeutic levels<sup>17-19</sup>. Aluminium exposure, apart from causing cholinotoxicity, can induce changes in other neurotransmitter levels since neurotransmitter levels are closely interrelated<sup>19</sup>. Al-Saleh and Shinwari<sup>20</sup> highlighted the adverse developmental effects of aluminium on children and infants. Antimony, on the other hand, has been found to induce DNA strand lesions but not DNA-protein crosslinks<sup>21</sup>. Fumes from melting antimony cause dermatoses and skin lesions<sup>22</sup>. Bearing in mind the reports on aluminium and antimony toxicity and many alarming reports on the association of kohl with lead poisoning in different countries, it was considered essential to examine the cosmetics found in Saudi Arabia. In this work we chose nine brands of the most expensive of mascara and eye shade from the Saudi market. Twenty eight elements were determined by using Inductively Coupled Plasma Mass Spectrometer (ICP-MS) and a flow injection mercury system (FIMS)<sup>23,24</sup>.

## MATERIAL AND METHODS

### Sample preparation

Accurately weighed portion (0.1 – 0.2g) of Mascara or Eye Shade sample was transferred to a TEFLON digestion tube (120 mL) and 7.0 mL of the acid mixture (HNO<sub>3</sub>/HF/HCl, 4.5:2:0.5) was introduced. The tube was sealed and the sample was digested inside a microwave oven (Milestone ETHOS 1600) following a heating program shown in Table 1.

After being cooled to ambient temperature, the tube was opened; 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 drive off the residual HF and HCl. The resulting digest was filtered in a polypropylene flask using 1% HNO<sub>3</sub> and made up to 50ml volume. For ICP-MS measurement the clear digest obtained were

diluted 10 times incorporating  $10 \mu\text{gL}^{-1}$  solution of  $^{103}\text{Rh}$ . In general, samples and standard reference materials (SRM) were prepared in a batch of six including a blank ( $\text{HNO}_3/\text{HF}/\text{HCl}$ ) digest.

### Chemicals and reagents

High purity water (DDW) (Specific resistivity  $18 \text{ M}\Omega\text{cm}^{-1}$ ) obtained from a E-pure water purification system (Barnsted, USA) was used throughout the work.  $\text{HNO}_3$ , HF and HCl used for sample digestion were of Suprapure® grade with certified impurity contents and were purchased from 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

Measurements were carried out by means of a Perkin-Elmer Sciex ELAN 6100 inductively coupled plasma mass spectrometer (ICP-MS). The instrument is equipped with a quadrupole mass filter, a cross-flow nebulizer and a Scott type spray chamber.

### Quality assurance

To assess of the analytical process and make a comparative analysis, Standard Reference Materials (Soile 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.

### Hg analyses

A flow injection mercury system (FIMS) from Perkin Elmer FIMS-400 was used for

determination of Hg in mascara and eye shade samples.

The FIMS is a complicated technique depending up on synchronization of mechanical, chemical and optical operations. The system contain 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.

The blank used in this process contained 2 v/v%  $\text{H}_2\text{SO}_4$ , 2v/v%  $\text{HNO}_3$  and approx.  $1.0 \text{ mg L}^{-1}$   $\text{KMnO}_4$  in de-ionized water. All the measuring standard and sample solutions were stabilized in the same medium.

## RESULTS AND DISCUSSION

There are currently no international standards for impurities in cosmetics. Limits have been established in Germany [25]. Rather than taking a risk-based approach, the German limits are based on levels that could be technically avoided. Thus, heavy metal impurities were limited to anything above normal background levels.

The German Federal Government conducted tests to determine background levels of heavy metal contents in toothpastes and other cosmetic products. Based on their studies, it was determined that heavy metal levels in cosmetic products above the values listed below are considered technically avoidable<sup>25</sup>:

**Table 1: Microwave heating program used for dissolution of sand, soil and sediment samples**

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

Lead: 20 ppm, Arsenic: 5 ppm, Cadmium: 5 ppm ,  
Mercury: 1 ppm , Antimony: 10 ppm

In Germany, a program is in progress to obtain updated values for traces of heavy metals in cosmetics<sup>26</sup>.

Health Canada has taken a similar approach in the establishment of heavy metal impurity limits, as the Department has always maintained that impurities in cosmetics should be reduced to the extent that is technically feasible. A

**Table 2: Concentration of elements in Soil 7**

Elements	Certifide Values 95% Confidence Interval in ppm	This work	
		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 3: The FIMS program**

Method name:	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 4: FIMS pumps 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 5: Levels of heavy metals in some facial cosmetics in some other parts of the world. (ND = Not detectable)

Country	Class/Name of cosmetics	Pb	Cd	Ni	Fe	Zn	Reference
Saudi Arabia	Henna	1.29 – 16.48 µg/g	-	-	-	-	[ 28 ]
Saudi Arabia, India, Middle East Morocco, US, Mauritania, Pakistan, India, UK and Saudi Arabia	Kohl, eyeliner pencils	2.9 – 100 % ND	-	-	-	-	[ 29 ]
Bulgaria	Kohl	0.6 – 50%	-		46%		[ 30 ]
Bulgaria	Eye shadow, lipstick and powders eye	ND -41.1 µg/g <20 µg/g shadows	-		-		[ 31 ]
Oman and UAE Bahrain	Bint al dhahab	~91%	~0.05%	-	-	-	[ 32 ]
UAE Bahrain	Suma and kohl	<0.16%	-	-	-	-	[ 33 ]
	surma	~88%					[ 34 ]
	kohl	~53%					[ 35 ]
Nigeria	Galena based kwali	58.8-62.4%	-		0.98-		[ 36 ]
	graphite-based kwali	23-32 µg/g	14-30 µg/g		1.2% . 0.43- 0.46%		[ 37 ]
Nigeria	Local eye shadows	-	-	-	6.15%	35 %	[ 38 ]





Table 6: Concentration of elements on the Mascara and Eye Shade samples (BDL = below detection limit)

	Brand 1			Brand 2			Brand 3					
	Mascara		Eye Shade	Mascara		Eye Shade	Mascara		Eye Shade			
	C4 (ppb)	rsd	C5 (ppb)	rsd	C12 (ppb)	rsd	C13 (ppb)	rsd	C20 (ppb)	rsd	C21 (ppb)	rsd
Li7	1600	2.6	99000	2.1	977	7.99	89000	1.7	1700	0.9	41700	3.3
B11	3500	7.1	20800	6.4			3E+07	1.5	6840		6840	9.4
Na	3E+06	0.6	986000	0.7	4E+06	1.26	2E+06	1.2	2E+06	1.2	1E+06	1.2
Mg	1E+06	1.0	5E+07	1.0	253000	1.09	2E+06	1.2	218000	1.1	3E+07	0.7
Al	4E+06	0.8	4E+07	1.2	4E+06	1.18	2E+07	1.1	2E+06	1.1	3E+07	0.9
K	789000	1.1	3E+07	0.9	633000	1.44	2E+07	0.3	988000	1.2	3E+07	1.0
Ca	305000	3.0	84500		455000	2.84	1E+06	7.0	753000	3.7	151000	8.5
V	143	7.5	10400	1.2	216	2.03	113000	0.9	451	1.7	9150	0.5
Cr	972	1.8	7E+06	0.9	3960	19.2	67700	0.3	17100	0.4	19200	0.8
Mn	72800	1.1	60900	0.6	182000	0.5	837000	0.7	536000	1.6	151000	1.0
Fe	3E+07	0.2	1E+07	1.4	6E+07	0.49	3E+08	0.4	9E+07	0.4	6E+07	1.0
Co	7190	0.7	1530	1.7	1730	1.64	31300	1.6	4650	1.8	2770	0.5
Ni	6520	1.4	6010	6.8	5760	1.27	112000	0.9	31400	0.4	29300	0.6
Cu			25700	1.8	640	1.62	14400	1.0	966	2.3	37300	0.5
Zn			2E+07	0.6	6890	2.94	84100	1.2	38600	0.8	101000	1.4
As	206	9.7	930	3.4	135	9.63	2540	6.3	605	5.5	929	10.2
Se			3410	22.7	102		427		1180		1230	12.7
Rb	3050	1.3	189000	1.2	4040	1.41	19400	0.9	6160	1.6	152000	0.6
Sr	8200	2.0	2390	1.3	7080	0.73	1550	0.8	6020	0.7	3460	0.2
Mo	121	8.9	1470	6.8			2000	3.0	220	2.4	273	2.1
Ag	50.9		135	4.8	29.4	10.5	27.1				412	3.2
Cd	17.1	10.1	266	5.8	2.18		16.9	14.4	26.9			
Ba	6270	1.4	53300	1.1	12800	2.81	35200	1.5	16200	7.1	77400	0.9
Pb	434	3.1	4410	0.2	576	1.34	5320	0.9	421	1.3	8090	0.5
U	285	1.7	897	1.3	200	1.64	149	3.3	38.7	4.7	691	2.8
Sb	11.6		159	16.1	30.2		167	11.4	24.7		129	4.2
Sn	19300	0.7	80100	0.3	19500	1.06	72300	0.6	22300	2.0	48900	0.5
Hg	9.5	5.2	8.2	2.4	2.6	6.5	4.2	2.4	1.5	10.6	0.18	



review and analysis of the results of heavy metal testing conducted in the Health Canada Product Safety Laboratory on a number of cosmetics sold in Canada lead to the determination of limits. Furthermore, comparison of conservative estimates of exposure to Canadians from use of cosmetics and the established tolerable intakes, demonstrated that these levels provide a high level of protection to susceptible subpopulations of consumers (e.g. children)<sup>26</sup>.

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. Heavy metal concentrations in cosmetic products are seen to be technically avoidable when they exceed the following limits:

Lead: 10 ppm, Arsenic: 3 ppm, Cadmium: 3 ppm, Mercury: 3 ppm, Antimony: 5 ppm

These levels are based on background levels found in cosmetic products sampled in Canada and are in line with acceptable levels of impurities in other jurisdictions. In addition,

**Table 7: the highest concentration of element among samples under investigation**

Element	Sample code	highest concentration in ppb
Li	C12 Mascara	263000
B	C67 Eye shade	3E+07
Na	C66 Mascara	4E+06
Mg	C59 Eye shade & C13 Eye shade	5E+07
Al	C30 Eye shade & C5 Eye shade	5E+07
K	C5 Eye shade	7E+07
Ca	C30 Eye shade	2E+06
V	C67 Eye shade	113000
Cr	C59 Eye shade	7E+06
Mn	C29 Mascara	5E+05
Fe	C20 Mascara	9.5E+07
Co	C67 Eye shade	31300
Ni	C40 Mascara	46800
Cu	C75 Eye shade	37300
Zn	C59 Eye shade	2E+07
As	C30 Eye shade	2950
Se	C59 Eye shade	3410
Rb	C30 Eye shade	2E+05
Sr	C13 Eye shade	41600
Mo	C67 Eye shade	2000
Ag	C29 Mascara	3760
Cd	C59 Eye shade	266
Ba	C13 Eye shade	2E+06
Pb	C5 Eye shade	11900
U	C5 Eye shade	3020
Sb	C30 Eye shade	2120
Sn	C30 Eye shade	1E+05
Hg	C58 Mascara	9.5

comparison of conservative estimates of exposure to Canadians from use of cosmetics and the established tolerable intakes for these metals demonstrated that these limits provide a high level of protection to susceptible subpopulations of consumers (e.g. children)<sup>26</sup>.

Levels of heavy metals in some facial cosmetics in some other parts of the world are shown in Table 5.<sup>27</sup>

Table 6 show the concentration of twenty eight elements on the Mascara and Eye Shade samples from the Saudi market. Comparing the results with the literature it is clear that lead, arsenic, cadmium, mercury and antimony level in the samples under investigation are within the normal level. The nickel concentration reach 46.8 ppm in sample C40. Aluminium concentration reach 5E+4

ppm in two samples C30 and C5. This concentration is high. In literature aluminium reach 5570 ppm in kohl sample<sup>35</sup>. Chromium is also reach high concentration in sample C59.

## CONCLUSION

Cosmetic in general may have a high concentration of element. Given the significant and relatively uncontrolled human exposure to cosmetic and their ingredients, these products must be thoroughly evaluated for their safety prior to their marketing<sup>36-38</sup>.

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