

Research Article

The Hazards of Hidden Heavy Metals in Face Make-ups

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Abstract: As a result of the widespread use of facial makeup many studies were reported for the determination of heavy metals in cosmetic products using different methods and instruments. Several facial cosmetics (powders and eyeliners) available in Sudan were analyzed for their contents of the heavy metals: arsenic, cadmium, lead and mercury. Samples were manufactured in different countries. The quantification of these heavy metals was performed by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). The analyses were preceded by microwave-assisted acid digestion of the products. The concentrations of the As and Cd are in the range of (2.376-6.796) and (0.2179-0.6179) ppm in the powder products and (1.504-4.084) and (0.1559-0.2959) ppm in the eyeliner products respectively. The Pb average (median) content is 3.288 and 0.0 ppm in the powder and eyeliner products. The mercury wasn't detected in any of the products analyzed. The percentages of the powder products analyzed contain As, Cd, Pb and Hg concentrations above the allowed limits are 81.8, 0.0, 9.1 and 0.0% respectively, but in the eyeliner products 50% of them contain Arsenic concentration above the allowed limit (3.0 ppm).

Keywords: Arsenic, cadmium, cosmetics, heavy metal, lead, mercury

INTRODUCTION

A cosmetic product is defined as being "any substance or preparation intended to be placed in contact with any part of the external surfaces of the human body (that is to say, the epidermis, hair system, nails, lips and external genital organs), or with the teeth and the mucous membranes of the oral cavity with a view exclusively or mainly to cleaning, perfuming, changing their appearance, protecting, keeping them in good condition or correcting body odours except where such cleaning, perfuming, protecting, changing, keeping, or correcting is wholly for the purpose of treating or preventing disease" (BIS, 2010). Cosmetic products include skin creams, lotions, perfumes, lipsticks, fingernail polishes, eye and facial make-up preparations, shampoos, permanent waves, hair colours, toothpastes, deodorants and any material intended for use as a component of a cosmetic product (FDA Cosmetics Handbook, 2010). According to the previous studies, we make this work to determine the amounts of heavy metals in some existing facial Make-ups types found in Sudan.

Toxicity of cosmetics: The amount of toxins in the environment has reached a level where the US FDA now has designated "permissible" levels of dioxin and other harmful chemicals in the environment, food and cosmetics. According to "National Geographic society

USA," studies, various chemicals in foods and environment indicate that man contributes 700,000 tons of pollutants into the air every day (Shirley, 1987), ranging from everyday household cleaners to cosmetics and hair dyes. The cosmetics are one of the main sources of toxins in environment. Today over 300 chemical toxins including dioxin were detected in human tissues that were not reported before (Shirley, 1987) February 3, 2005 the Food and Drug Administration issued an unprecedented warning to the cosmetics industry stating that the Agency is serious about enforcing the law requiring companies to inform consumers that personal care products safety has not been documented, but the safety of the ingredients in these products is looked into almost exclusively by a manufacturer-controlled safety committee called the Cosmetic Ingredient Review (CIR) panel (Shirley, 1987). In this study we focus on toxicity of heavy metals in cosmetics, Heavy metals are metallic elements which have a high atomic weight and a density much greater (at least 5 times) than water. In small quantities, certain heavy metals are nutritionally essential for a healthy life as the building blocks of our bodies. They are required for body structure, fluid balance, protein structures and to produce hormones. They act as co-factors, catalysts or inhibitors of all enzymes in the body. Copper and iron, for example, along with other minerals are required for the electron transport system and thus needed for all cellular energy

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production (Lawrence, 2012). 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 disease, 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 for some heavy metals (CIS, 1999). Toxic levels can be just above the background concentrations naturally found in nature. Therefore, it is important for us to promote our knowledge on the heavy metals toxic effects and on the protective measures against excessive exposure.

Determination of heavy metals in cosmetics:

Environmental defense Canada studied 49 items of different makeup for a total of eight different heavy metals (Arsenic As, Cadmium Cd, Lead Pb, Mercury Hg, Nickel Ni, Beryllium Be, Thallium Tl and Selenium Se). Twenty of the products were manufactured in the United States, ten in Europe, four in Canada and one in Korea. None of these metals were listed on the products labels (Environmental Defence Canada, 2011). Seven of the eight metals of concern were found in 49 different face makeup items. On average two of the four metals are present in any of those products. But results varied for each product. Arsenic was detected in 20% of the products, cadmium in 51% and lead in 96%. Nickel, beryllium, thallium and selenium were found in 100, 90, 61 and 14% of all items, respectively. The results described above obtained by using microwave system digestion for preashed samples and then were analyzed by ICPOES and ICP-MS (Lee *et al.*, 2008). Another method was developed for multi element analysis of sunscreen creams and lotions by using an Inductively Coupled Plasma Atomic Emission Spectrometric (ICP-AES) method and standard addition. The objective was the simultaneous determination of Titanium dioxide (TiO_2 being is the only authorized inorganic UV filter in the European Union) and several elements (Al, Zn, Mg, Fe, Mn, Cu, Cr, Pb and B) in the final products. Two alternative pretreatment procedures were reported:

- Total wet acid digestion in closed pressurized vessels by three acid mixtures
- Direct introduction of sample in the form of emulsified slurry (Zachariadis and Sahanidou, 2009)

The recoveries of the proposed acid digestion method were evaluated using spiked samples. The calculated recoveries were 95.0% for Ti, 98.2% for Zn

and 101.3% for Fe and the lower detection limits were $0.2 \mu\text{g g}^{-1}$ for Ti, $0.2 \mu\text{g g}^{-1}$ for Zn and $0.5 \mu\text{g g}^{-1}$ for Fe. One of the tested samples contains titanium dioxide with aluminum in the form of alumina and aluminum stearate, as it is listed on the product label. Alumina is commonly used to improve the properties and skin compatibility of titanium dioxide. A second sample based on titanium dioxide UV filter, without alumina. A third sample was also tested contains high Magnesium (Mg) concentration as magnesium stearate in order to improve the dispersion properties of titanium dioxide (Zachariadis and Sahanidou, 2009). A study evaluated the content of heavy metals in samples of eye shadows manufactured in different countries (China, Italy and USA). The content of Pb was measured by Flame-Atomic Absorption Spectrometry (F-AAS). The quantification of cadmium, cobalt, chromium and nickel was performed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The analysis was preceded by microwave-assisted acid digestion of the eye shadows. Five brands and 20 colors of eye shadow samples were analyzed. The results for lead varied considerably 0.25 to 81.50 $\mu\text{g/g}$, Cadmium level ranged from 0.60 to 33.04 ng/g . Seventeen out of 20 of the colors had cadmium level below 10 ng/g (Volpe *et al.*, 2012). In most cases, cobalt content varied between 0.65 and 8.47 ng/g . The highest results of cobalt were 303.7, 180.5 and 161.0 ng/g . Chromium was measured in the range of 15.0 to 287.0 ng/g . Most of the nickel levels ranged between 21.8 and 145.2 ng/g . In many samples the lead was present within the level permitted in cosmetics for external use, but it exceeded this limit in four Chinese samples. The levels of cadmium, chromium and cobalt were low and within acceptable concentrations for the products made in USA and Italy, but the nickel concentration exceeded the safe limit in many Chinese eye shadows. The overall results indicate that eye shadows are manufactured according to different regulations in different countries and Chinese products are likely to be more harmful (Volpe *et al.*, 2012).

Arsenic: Arsenic is found in nature at low levels. It's mostly in two compounds, one with oxygen, chlorine and sulfur (inorganic arsenic compounds) and other in plants and animals combines with carbon and hydrogen (organic arsenic) (www.tuberoso.com, 2011). Arsenic is called the slow death mineral. Its symptoms are vague. Because it is colorless and tasteless it was added to food and hence leads to slow death (Lawrence, 2012).

Cadmium: Cadmium is a natural element in the earth's crust. It is usually found as a mineral combined with other elements such as oxygen (cadmium oxide), chlorine (cadmium chloride), or sulfur (cadmium

sulfate, cadmium sulfide) (www.tuberos.com, 2011). Cadmium does not corrode easily and has many uses: in industry, consumer products, batteries (Ni-Cd batteries of mobile phones), pigments, metal coatings and plastics (Health Canada's Draft Guidance on Heavy Metals in Cosmetics, 2011). Cadmium is classified as a human carcinogen by the National Institute for Occupational Safety and Health (NIOSH) (Guy *et al.*, 1999), International Agency for Research on cancer (IARC, 1997) and by the United States Department of Health and Human Services (Agency of Toxic Substances and Disease Registry, 2008).

Absorption of cadmium through the skin is low (0.5%) and would be of concern only in situations where concentrated solutions would be in contact with the skin for several hours or longer. Cadmium binds to epidermal keratin when applied topically, thus explaining the limited dermal absorption observed. However, significant dermal exposure, as could occur in an occupational setting, can cause irritant dermatitis (Guy *et al.*, 1999).

Lead: It can be found in all parts of our environment. Every year, industry produces about 2.5 million tons of lead throughout the world. Most of it came from human activities like mining, manufacturing and the burning of fossil fuels (Lawrence, 2012), mainly in manufacturing tetraethyl lead for constructional purposes in manufacturing sulfuric acid; in manufacturing phosphoric acid, chlorination or sulfonation processes, petro refining, gas production, extraction, condensation; manufacturing various chemical equipment: pipes, valves, stirrers, coils, kettles, pumps, evaporators, condensers; for lining tanks of various electroplating solutions (Theodore, 2012).

Mercury: Mercury can be present in every place e.g., Primary mercury mines, by-product recovery from other mining, decommissioned chlor-alkali plants, recovered mercury from wastes and products and government stockpiles (only U.S. stockpile remains (CIS, 1999). Mercury compounds were added to paint as a fungicide until 1990. These compounds are now banned; however, old paint supplies and surfaces painted with these old supplies still exist (Health Canada. It's Your Health: Effects of Lead on Human Health, 2008). Medicines, such as mercurochrome and Merthiolate, are still available. Mercury salts are used in skin-lightening creams and as antiseptic creams and ointments.

MATERIALS AND METHODS

Samples of Eleven powders and four eyeliners of different brands were purchased from a local open market. Every sample label contained the manufacture

country of origin. Samples were stored at room temperature waiting analyzed.

Materials:

- Arsenic calibration standard solution 1000 ppm in hydrochloric acid (Fisher Scientific, UK)
- Cadmium calibration standard solution 1000 ppm in nitric acid (Fisher Scientific, UK)
- Lead calibration standard solution 1000 ppm in nitric acid (Fisher Scientific, UK)
- Mercury calibration standard solution 1000 ppm in Hg (NO₃)² (Chem. Lab NV)
- Nitric acid 65% (Scharlau, Spain)
- Hydrochloric acid 37% (Scharlau, Spain)
- Hydrogen peroxide 30% (Scharlau, Spain)
- Deionized water
- Whatman filter papers (ashless papers 125 mmΦ)

Determination of metals concentration: Fifteen samples (11 powders and 4 eyeliners) were purchased from the different markets. From each of samples one (0.20 g) was weighted using well calibrated high sensitive balance (Wag tech) in high pressure resistance microwave vessel (made of Teflon). According to ASEAN method (ASEAN Association of Southeast Asian Nations), to each sample 6 mL of nitric acid, 1.5 mL of hydrogen peroxide and 2 mL of hydrochloric acid were added sequentially by using a graduated pipette, then the vessels were closed tightly and left for 15 min to ensure complete reaction. The samples were then digested using clearly washed and calibrated microwave digestion instrument (START D, Milestone).

By using calibrated ICP-OES instrument the concentration of the metals (As, Cd, Pb and Hg) were determined in the 15 samples (powders and eyeliners).

RESULTS

The Concentration of Elements (As, Cd, Pb and Hg) (ppm) in the products as was shown in Table 1 and Fig. 1 to 4. The concentrations of the As and Cd are in the range of (2.376-6.796) and (0.2179-0.6179) ppm in the powder products and (1.504-4.084) and (0.1559-0.2959) ppm in the eyeliner products, respectively. The Pb average (median) content is 3.288 and 0.0 ppm in the powder and eyeliner products. The mercury wasn't detected in any of the products analyzed. The percentages of the powder products analyzed contain As, Cd, Pb and Hg concentrations above the allowed limits are 81.8, 0.0, 9.1 and 0.0%, respectively, but in the eyeliner products 50% of them contain Arsenic concentration above the allowed limit (3.0 ppm).

Table 1: The concentration of elements in the powders (ppm)

No. of sample	As ppm	Cd ppm	Pb ppm	Hg ppm
1	7.618	0.2647	6.6510	0.00
2	4.038	0.6198	0.0132	0.00
3	7.127	0.3735	3.2880	0.00
4	4.814	0.2088	0.6082	0.00
5	3.045	0.3109	3.1340	0.00
6	2.667	0.2264	11.0340	0.00
7	4.199	0.6695	6.0400	0.00
8	5.803	0.3060	1.9930	0.00
9	6.629	0.6777	8.0610	0.00
10	0.000	0.6873	3.4040	0.00
11	4.512	0.6873	1.7710	0.00
Mean±S.D.	4.586±2.210	0.4179±0.2000	3.2880*	0.00

*: The mean was not valid as indicated by the S.D. and the shown result represents the median

Table 2: The concentration of elements in the eyeliners (ppm)

No. of sample	As ppm	Cd ppm	Pb ppm	Hg ppm
1	4.655	0.2731	0.000	0.00
2	2.675	0.1388	4.287	0.00
3	1.819	0.1965	0.000	0.00
4	2.029	0.2952	0.000	0.00
Mean±S.D.	2.794±1.290	0.2259±0.0700	0.000*	0.00

*: The mean was not valid as indicated by the S.D. and the shown result represents the median

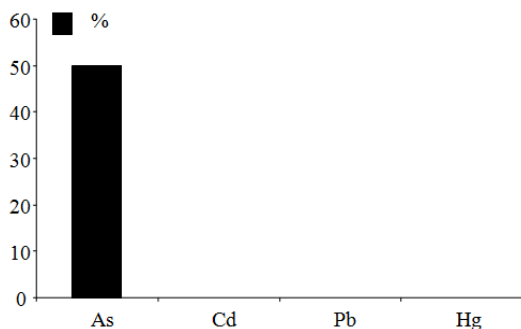


Fig. 1: The percentages of the eyelineer products containing heavy metals concentration above the allowed limits

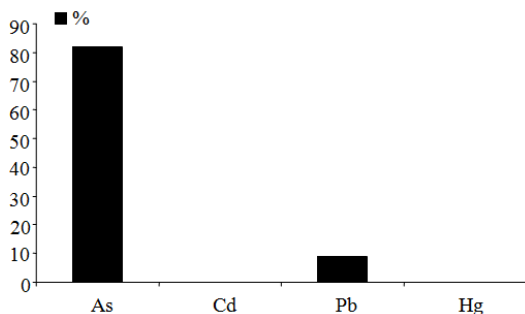


Fig. 2: The percentages of the powder products containing heavy metals concentration above the allow limits

DISCUSSION

The use of cosmetics is becoming almost everybody's daily habit today applying one or more of facial cosmetics creams, powders, eyeliners, foundations, concealers, eye shadows, mascaras and

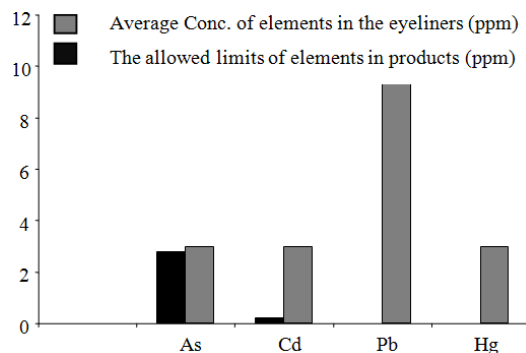


Fig. 3: The averages concentration of metals in the eyelineer products compared to allowed limits

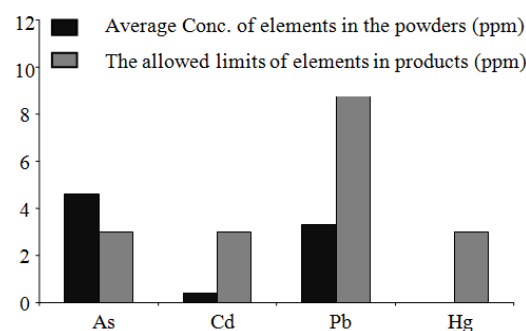


Fig. 4: The averages concentration of metals in the powder products compared to allowed limits

lipsticks or glosses. Although most of the present face make ups are containing heavy metals, however, consumers have often no way of knowing about these metal contents. The distribution of trace metals in the facial cosmetics (powders and eyeliners) studied described in Table 1 and 2 shows that the levels of Arsenic (As) are generally high to the extent of being greater than the allowed limit of 3.0 ppm (2.376-6.796) as for nine of the studied powder brands, but in eyeliners only one brand above the allowed limit. Such high levels of arsenic often constitute a health hazard to users as compared to the published reports (Health Canada's Draft Guidance on Heavy Metals in Cosmetics, 2011). The levels of Cadmium (Cd) in the studied samples are all below the allowed limit of 3.0 ppm in the range of (0.2179-0.6179) and (0.1559-0.2959) for powders and eyeliners respectively and hence unlikely to represent a health risk. The levels of Lead (Pb) are widely scattered to allow the calculation of a mean value. However, the median values are 3.288 and 0.0 ppm for powders and eyeliners respectively. Showing only one powder product with a level greater than the allowed limit of 10.0 ppm (Table 1). Mercury a widely used element in most cosmetics as skin-lightening creams and as antiseptic creams or ointments has not been detected in the studied samples. This result is mainly attributed to the high volatility of mercury

particularly under the experimental conditions of our method namely the high temperature microwave assisted acid digestion technique. This metal requires special treatment for digestion to prevent its evaporation as previously reported (cold vapor extraction) (William and Maria Gomez, 2001). Unfortunately we failed to develop this cold vapor extraction method in Sudan due to the unavailability of the required equipment. Although many of the studied samples have metals concentrations within or below the allowed limits, however, the reported use of these cosmetics would be expected to lead to the metals build-up in the user's bodies overtime and hence consequent development of risks and health hazards. Significant concentrations of metals upon repeated applications of cosmetic products have been reported in body fluids in previous studied (Sin and Tsang, 2003). It shouldn't be surprising that heavy metals in makeup's although they are often measured in parts per million, however, they are areal cause of concern if we consider the levels of exposure for which the margins of safety have not been established. Cumulative exposure over time is especially difficult to study, as different combinations of exposure can have different effects, as well as the fact that the possible combinations are seemingly endless. Additionally cosmetics are not the only source of exposure to many of these metals. Arsenic e.g., can be found in same drinking water, mining sites and lead in old paints, left-out dry batteries etc. and hence low-dose exposures adding up wouldn't be unexpected.

Furthermore facial cosmetics, such as those applied to lips ingested as well as some may also be absorbed through the skin, especially broken skin (Chris, 2010). Eliminating elements like lead and cadmium from the body takes over 40 years, with accumulation leading to problems such as nervous system disruption and kidney damage. According to the United States Centers for Disease Control (CDC) (2010), there is no known safe blood lead level; even the current "low" levels of exposure in children are associated with neuro developmental deficits (Bellinger, 2008). The CDC has even gone so far as to recommend that parents avoid using cosmetics on their children that could be contaminated with lead (Centers for Disease Control and Prevention, 2009). Heavy metals are in our face makeup while not intentionally added, they remain unlabelled on products and we therefore unknowingly put them on our eyes, face and lips. The good news is that some of the products tested contained lower levels of heavy metals of concern than others. But, consumers have no way of knowing short of sending face makeup to a lab for testing if their products contain metal impurities and at what levels. The amounts applied to the skin or lips each day might be small, but exposures via cosmetics and elsewhere can add up over time.

CONCLUSION

The application of ICP-OES techniques allowed the quantification of heavy metals in facial cosmetics (powders and eyeliners). In many samples the Arsenic was present in high level than Canadian limit. The levels of cadmium and Lead were always low and within acceptable and safe concentrations for the products analyzed. The overall Results indicate that powders and eyeliners are likely harmful due to accumulation of these metals in the body. Therefore, we need to recommend major quality controls for products designed to enter in direct and long contact with the skin when imported from different countries.

RECOMMENDATIONS

This research study was restricted to certain aspects of facial cosmetics due to time and resources restrictions, but could be extended to cover more cosmetic products as well as their effects in human. It is also of paramount importance to establish in the country a laboratory facilities that could allow the detection of mercury being one of the common components in cosmetic products as well as it's presence in the environment. Need is urgent for the establishment of the cold vapor extraction technique in our laboratories. Promotion of public awareness particularly among the regular users of cosmetic products about their likely health risks. Periodical analysis of heavy metals levels should be encouraged on personal and family-scale.

ACKNOWLEDGMENT

Our sincere gratitude and thanks are extended to the staff members of the Faculty of Pharmacy, Sudan International University and to everyone at the university of Medicinal science and technology, who assisted us in one way or another during our research.

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