DOI: 10.7251/QOL1701023J **UDC:** 546.19:541.135

Original scientific paper

Arsenic and Mercury Content Determination in Commercial Cosmetics Products by Atomic Absorption Spectroscopy

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Abstract: Toxic elements are present everywhere in nature and even in raw materials and pigments used in the manufacture of cosmetics. Human bodies daily exposed to toxic elements that can be found in trace amounts in cosmetic products. These elements such as arsenic and mercury can cause local skin damage or possible, their absorption through the skin or swallowed. In this paper we determined the content of arsenic and mercury in ten lipstick samples and eight nail polishes samples by atomic absorption spectroscopy (AAS). Acid digestion with 0,1 M HCl or HNO_3-HCl was performed. A very low concentration of Hg and As have been found in all samples in both extracts (ranged, 0.0001-0.0004 µg/g and 0.02 – 0.04 µg/g respectively).

Keywords: toxic element, arsenic, mercury, cosmetics

Introduction

Due to very intensive and technological industrial development, a lot of harmful and toxic substances are introduced into atmosphere. A great part of those hazardous and toxic substances are classified as heavy metals. About 80 elements in periodic table have been classified as metals, and among them 30 metals can have toxic effects on humans. Heavy metal is every metal that have density higher then $5 g/cm^3$ (Jokanović, 2010).

There are two ways for infiltration of heavy metals in environmental, a natural and the anthropogenic one. Plants have ability to absorbs heavy metals through its root or heavy metals can be deposit from air on the leaf of a plant. In this way, heavy metals are included in food chain, since human and animals eat plants.

In normal conditions, there are three ways of entrance of heavy metals in the body: through the skin, gastro-intestinal tract and *via* the respiratory tract. Distribution of heavy metals through the body is carried out with the blood (or lymphoma), and some of them show affinity for binding to the red blood cells (such as organic compounds of As and Hg) or to plasma proteins (inorganic compounds Hg) while some may bind to leukocytes (Zn). They have the ability to pass through a natural barrier, the blood-brain organism (included in the CNS) or placenta (acting on the fetus). Mainly the heavy metals are deposited in the target organ, such as bones, kidneys, liver or brain. Excretion is done through the respiratory tract, the salivary glands (lead, mercury and cadmium), through the skin, sweat and sebaceous glands. The most significant amounts of heavy metals are excreted *via* the urine and the digestive tract (Jokanović, 2010)

It is very important to emphasize that heavy metals are dangerous because they have the potential of bioaccumulation. There is clear evidence that some metals can cause carcinogenic effects in humans and animals. The International Agency for Research on Cancer classifies arsenic, beryllium, cadmium, hexavalent chromium and nickel compounds in the compounds for which there is sufficient evidence that they are carcinogenic to humans. Cases of skin cancer in people who were exposed to arsenic compounds have been described even in the nineteenth century. Carcinogenic effects metals are particularly important due to their widespread distribution (Jokanović, 2010; Chung, Yu and Hong 2015).

Arsenic present in drinking water is considered to be one of the most important causes of cancer in the world. In 1963, World Health Organization (WHO) recommended maximum allowable concentration of arsenic in drinking water and they were 50µg/L. In 1992. WHO reduces arsenic level up to 10 µg/l, for there was clear evidence that arsenic presence is connected to cancer risk. There was a direct correlation between the presence of inorganic arsenic in drinking water and cardiovascular disease (Chung et al., 2015). The impact of arsenic on the vascular system has also been reported in a number of other populations. It was also shown that there is a link between the presence of arsenic in drinking water and diabetes.

Mercury in cosmetics exists in two forms: inorganic and organic. Inorganic Hg are absorbed through the skin and excreted primarily via the kidneys, and elevated urinary Hg concentrations have been associated with signs and symptoms of Hg poisoning (Bocca, Pino, Alimonti and Forte, 2014). The Regulation EC1223/2009 and the Council Directive 76/768/EEC specify that Hg and its compounds are not allowed as ingredients in cosmetics (EU, 2009). The US FDA (2000) allowed Hg compounds in eye area cosmetics at concentrations at or below 65 µg/g while all the other cosmetics must contain Hg at concentration less than 1 µg/g (FDA, 2000). In Germany, the Hg limit as impurity in cosmetic is also 1 µg/g (BfR, 2006). Regulation in Republic of Srpska proposed Hg limit is 5 µg/g in lipsticks and in eye shadows is 10 µg/g and for As 5 µg/g in both cosmetics products (Anon., 2015).

Materials and Methods

Samples were purchased in stores in Banja Luka in December 2016. For analysis of mercury and arsenic ten samples of lipstick and eight samples of nail polish were chosen. Cosmetics samples were produced by 14 different manufacturers. All samples were stored at room temperature until analysis.

The 65% nitric acid and 35% hydrochloric acid used for digestion were of suprapure quality (Merck Darmstadt, Germany). The Mercury and Arsenic standards were prepared from commercial 1000 ppm solutions (Perkin Elmer).High purity deionized water was used for dilution of standards and samples.

Atomic absorption spectroscopy was performed by Perkin Elmer Analyst 400 instrument with MHS-15 Mercury/Hydride System. This system is a manual accessory for high-sensitivity determination of mercury and hydride-forming elements such as As, Se, Sb, Te, Bi and Sn, by flame atomic absorption (AA) spectroscopy.

Sample Preparations

Extraction Hg and As from lipsticks and nail polishes samples was carried out parallel with two solutions: 0,1M HCl and *aqua regia* (HNO_3 : HCl 1:3).

Aliquots of each sample were weight in the glass vessels. About 1 g of samples were weighed in the case of extraction with 0,1M HCl and about 0,5 g of samples were weighed in the case of extraction with *aqua regia*. A solution of 50 mL of 0,1 M HCl was added to each vessel and then boiled for 15 min under reflux. After cooling samples were passed through quantitative filter papers (Whatman No 42) in 50 mL volumetric flask and diluted with 0,1M HCl. The samples were then transferred to plastic bottles, previously washed with 30% HNO_3, and stored in a refrigerator until analysis. These solutions were used for determination of mercury content.

Solutions for determination of As were pre-reduced (As^{5+} to As^{3+}) prior analysis. This was achieved by adding a reducing solution containing 5% (w/v) KI and 5% (w/v) ascorbic acid. A 10 mL of solution which we used for determination of mercury was transferred in 50 mL volumetric flask and added 1 mL of 5% KI and 1 mL ascorbic acid. Finally, solution was made up to mark with 2M HCl.

Results and discussions

Arsenic and mercury concentrations contained in lipstick and nail polishes are summarized in Table 1. and Table 2. Observed concentration of As and Hg in all analyzed cosmetics samples were very low. In all analyzed lipstick samples and five samples of nail polishes, which were digested with 0,1 M HCl, content of As was below the LoD. In *aquaregia* extract, content of As was slightly higher but still it was below of detection limit in 4 samples of lipstick and 2 samples of nail polishes. Maximum arsenic content was 0.04 µg/g in nail polish sample, number 6, red color, both in HCl extract and *aqua regia* extract. Arsenic in lipstick showed very low levels in three different studies, minimizing the possible exposure scenario (Grosser, Davidowski and Thompson 2011). Similar low values were found by Al-Aleh and Al-Enazi (2011) with the exception of one chocolate colored product (6,52 µg/g). On the contrary, higher values were reported in lipsticks tested in New Zealand, 68 of them containing As from 1.1 to 5 µg/g and 18 products between 5.1 and 9.0 µg/g (CPHR, 2011).

Data reported in Table 1 and Table 2 show very low levels of Hg in cosmetics. Content of Hg was in the range of 0.0001-0.0004 µg/g. Literature data have showed that due to the high demand for use skin-lightening creams, extremely high levels of Hg could be found in Mexico (ranged, 8.79-35.824 µg/g) (Peregrino, Moreno, Rubio and Leal 2011) and Saudi Arabia (ranged, 0.09-5650 µg/g) (Al-Saleh and Al-Doush 1997). This is potentially dangerous for health taking into account that the safe US FDA (United States Food, Drug and Cosmetic Act) limit is 1 µg/g. Other types of cosmetics such as lipsticks, nail polishes, mascara, eye shadows, shampoo, hair conditioners, etc., had values of Hg very low or under the analytical methods limit (Adepoju-Bello et al., 2012; Al-Saleh, Al-Enazi 2011; CPHR, 2011; Grosser et al., 2011).In our country safe limit for Hg content in lipstick is 5 µg/g. The maximum allowed content of Hg in the nail polishes is not defined by law of Republic Srpska.

Table 1. Content of As and Hg in lipstick samples

Sample number	Brand	Shade	Production country	As (µg/g)		Hg (µg/g)	
				0,1M HCl	Aqua Regia	0,1M HCl	Aqua Regia
1	Max Factor	red	Ireland	<0.02	<0.02	0.0002	0.0001
2	Catrice	red	Italy	<0.02	<0.02	0.0001	0.0002
3	Catrice	purple	Italy	<0.02	<0.02	0.0003	0.0002
4	L´Oreal	rose	Italy	<0.02	<0.02	0.0004	0.0003
5	Rimmel	dark red	England	<0.02	0.02	0.0002	0.0002
6	Rimmel	light rose	England	<0.02	0.02	0.0001	0.0001
7	Art Deco	red	Germany	<0.02	0.02	0.0001	0.0001
8	Bourjois	red	France	<0.02	<0.02	0.0001	0.0001
9	Deborah Milano	orange red	Italy	<0.02	<0.02	0.0001	0.0002
10	Catrice	red	Italy	<0.02	0.03	0.0001	0.0001

Table 2. Content of As and Hg in nail polishes samples

Sample number	Brand	Shade	Production country	As (µg/g)		Hg (µg/g)	
				0,1M HCl	Aqua Regia	0,1M HCl	Aqua Regia
1	Evelin	rose beige	Polish	<0.02	<0.02	0.0001	0.0001
2	Maybelline	red	Italy	<0.02	<0.02	0.0001	0.0001
3	Miss sporty	purple	United Kingdom	<0.02	0.02	0.0001	0.0001
4	Golden Rose	dark red	Turkey	<0.02	0.02	0.0001	0.0002
5	L´Oreal	beige	Italy	<0.02	0.02	0.0002	0.0002
6	Misslyn	red	Germany	0.04	0.04	0.0001	0.0001
7	Golden rose	red	Turkey	0.02	0.03	0.0001	0.0001
8	Maybelline	rose	Italy	0.02	0.03	0.0001	0.0002

Conclusions

We examined presence of Arsenic and Mercury in ten samples of lipsticks and eight samples of nail polishes by atomic absorption spectroscopy. Content of these toxic elements was very low or under the analytical methods limit in both extracts. None of the lipsticks samples exceeded the maximum limit which proposed by law of Republic of Srpska. Maximum limit of As and Hg in nail polishes is not defined by law of our country. Arsenic, As-compounds, Mercury and Hg-compounds are prohibited ingredients in cosmetics in Europe but impurities of these elements can be found in the row material or can be accurate during the production of cosmetic. Although these are very small amounts and they are not label on a package, consumers must be aware of the possible risk. There are many cosmetics products on the market that are used daily to the skin, eye, lips, nails and impurities such as As and Hg and other toxic elements accumulate in the body over time and this is what should be taken into account for setting maximum permissible limits of toxic elements in cosmetics products.

Acknowledgments

This work was done within the framework of the research project no. 19/06-020/961-26/15 supported by the Ministry of Science and Technology of Republic of Srpska

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Recived: 30.4.2017.

Accepted: 10.6.2017.