

ASSESSMENT OF CADMIUM CONTENT IN COSMETICS BY EXTRACTION WITH DILUTED HCl AND AQUA REGIA

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Abstract: The intensive industrial and technological development results in an appearance of a large amount of pollutants and toxic substances in the biosphere including large quantities of heavy metals. Some heavy metals are biogenic (Cu, Zn, Se etc.) and essential for proper maintaining of the metabolism in the human body. The main dangers to the human health are associated with the exposure to toxic elements such as Pb, Cd, Hg and As. Emission of Cd in the environment has increased during the 20th century mainly due to the recycling of the products containing this element. Cadmium accumulates in the human body with a biological half-life from 10 to 30 years and could cause very serious toxic effects. Cosmetic products are potentially a source of cadmium as well as some other heavy metals mostly due to the frequent and uncontrolled usage of cosmetics of poor and/or suspicious quality. The goal of the study is to determine the cadmium content in various cosmetic products (lipsticks, eyeshadows and blushes) present in the markets of the Republic of Srpska. The content of Cd was determined with atomic absorption spectrophotometry (AAS) after the extraction with diluted HCl and aqua regia. The results of the research show that the cadmium concentrations in the investigated products are in accordance with the regulations of the Republic of Srpska (Regulations on safety of consumer goods; „Official Gazette RS“ – No.17/15).

Keywords: cadmium, cosmetic, atomic absorption spectrophotometry, legislation.

1. INTRODUCTION

From the beginning of civilization, cosmetics has been utilized by people in the various forms. Cosmetics is any substance or preparation intended to be placed in contact with various external parts of human body (epidermis, hair, lips etc.) or applied to the teeth or muscous membranes of the oral cavity mainly for purpose of cleaning, protection and beautification [1,2]. Raised consciousness of the body care and beauty resulted in variety of cosmetic products used in everyday routine [3].

Cosmetic products contain a lot of different chemical compounds, among them heavy metals and their compounds have a special place. The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic by low concentrations [4]. Heavy metals might not cause

immediate health problems, but their cumulative effect due to repeated application of cosmetics cannot be ruled out. The main dangers to the human health are associated with the exposure to toxic and harmful elements such as Pb, Cd, Hg and As.

Since majority of cosmetic products are applied to the skin, the heavy metals from them are mostly absorbed through skin. Dermal absorption of heavy metals is typically low. Second path of the metals from the cosmetic to the human body is oral. Oral exposure can occur to cosmetic used in and around the mouth, such are lipsticks, as well as from hand-to mouth contact after exposure to cosmetic. Inhalation exposure by metals from cosmetic is expected to be negligible [5].

According to the International Agency for Research on Cancer, cadmium and its compounds were classified as cancerogenous -group 1 since

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1993 [6]. Cadmium targets are blood vessels and heart tissue as well as kidneys, lungs and brain, and results in heart disease, hypertension, liver damage and suppressed immune system. Cadmium also causes bone degradation because of influence onto calcium metabolism [7,8]. Cadmium has an extremely long residence time inside of the human body. The accumulation of cadmium in the kidney increases along with age, suggesting that cadmium exposure will adversely affect health, particularly in older age groups. Inhalation of this element causes pulmonary infection, with cigarette smoke being a significant source of Cd [9].

There is a growing concern about the dangers of cadmium in the environment, mostly because of its toxicity and broad application in industry and recycling of the products. Cadmium is by-product of the Zn industry, which is recovered from the smelting and refining of the zinc concentrates [8]. Cadmium is mainly used in production of rechargeable (nickel-cadmium) batteries, pigments, coating and plating, manufacture of plastic products and alloys [7]. The use of cadmium in cosmetic products is due to its colour pigments.

Quality of the cosmetic products in Republic of Srpska is regulated through Regulations on safety of consumer goods. According to this regulation, products used for the beautification and coloring the mouth (e.g. lipstick) should not contain more than 2 mg Cd/kg. Products used for the beautification and coloring the eyes and eye area and other decorative cosmetics, accepting the cosmetics for the hair and nail, should not contain more than 5 mg Cd/kg [10]. The maximum permitted values according to before mentioned regulations are defined for the contents of Cd detected in cosmetic products after extraction with dilute hydrochloric acid ($c=0,1$ mol/L). There is prohibited any presence of cadmium in cosmetic products inside of the EU countries [11]. On the other side, maximum allowed level of Cd in cosmetics in Canada is 3 mg Cd/kg [5].

However, no known investigation has been done before about the presence of cadmium in the cosmetic products sourced from markets in Republic of Srpska. Because of that, the goal of this study was determination of the cadmium contents in some of the most commonly used cosmetic products: lipsticks, eye-shadows and blushes. These three products are facial make-up mostly applied by women. During this research, some of the most common and price acceptable cosmetic products have been examined inside of this group found in the cosmetic shops in Banja Luka.

2. MATERIAL AND METHODS

Fifteen samples of the most popular brands of lipsticks, eyeshadows and blushes, five of each mentioned product, were collected in the several cosmetic shops from local markets in Banja Luka. All of the collected cosmetic samples were within shelf life. The samples were firstly labeled and the general characteristics such as name of product, brand, colour etc. have been recorded. The extraction of cadmium (Cd) from the investigated cosmetic products was done parallel with two different solutions: diluted hydrochloric acid ($c=0,1$ mol/L) and aqua regia (conc. HNO_3 : $\text{HCl}=1:3$).

During the extraction with diluted hydrochloric acid, $1,00 \pm 0,01$ g of the investigated samples was weighted in the glass vessels. In each vessel, 50 mL of the HCl solution ($c=0,1$ mol/L) was added and afterwards boiled during 15 minutes under reflux. After cooling, the obtained solutions were passed through quantitative filter paper (Whatman No. 42) into volumetric flasks ($V=50$ mL) which were filled with the hydrochloric acid solution to the mark.

Digestion with the aqua regia was done with $0,50 \pm 0,01$ g of the samples and 10 ml of the solution. After 30 minutes of boiling in the glass vessels under reflux, the obtained solutions were cooled on the room temperature and afterwards were filtrated (Whatman No. 42) into 50 mL volumetric flask. The solutions were diluted up to the mark by deionized water. The extracts obtained after both described extraction procedures were transferred to the plastic bottles, prewashed with 30% HNO_3 and stored in refrigerator ($t=4^{\circ}\text{C}$) till further analyses.

Determination of the cadmium content inside of the extracts was done by method of atomic absorption spectrophotometry using the instrument AAnalyst 400 Perkin Elmer. All the measurements were carried out in duplicates. The cadmium content was determined on the wave length of 228.80 nm, using the air/acetylene flame and background correction of signal with deuterium lamp. The calibration equation was linear through zero. The calibration curves, for the both extractants, were constructed with five points (one blank and four standards) and its correlation coefficients were $>0,995$ before the sample analysis. Standard solutions with the concentrations of 0.2, 0.5, 0.7 and 0.9 mg Cd/L were prepared by serial dilutions of the standard stock solution (1000 ppm, Perkin Elmer).

The 65% nitric acid and 35% hydrochloric acid used for extraction and preparation of the

working solutions were suprapure quality (Merk Darmstadt, Germany). All the dishes used during the analyses were prewashed by leaving during the night in the 10% HNO₃. High purity deionized water was used for dilution of solutions and washing the dishes.

3. RESULTS AND DISCUSSION

Determined concentrations of cadmium in all investigated cosmetic samples were very low (Table 1). The content of cadmium in all lipstick samples (Table 1) after digestion with diluted HCl was less than limit of detection (0,01 mg/kg), with exception of the sample number 5 where 0,05 mg Cd/kg have been found, what is lower from maximum limit value by our regulation, 2 mg Cd/kg [10]. In aqua regia extracts, content of Cd was similar like in the diluted HCl extracts. Maximum cadmium content (0,26 mg Cd/kg) was found in the aqua regia extract

obtained from the sample number 5. This value is also far from the allowed maximum in our country [5,10]. Hepp et al. have not found any cadmium in the 30 examined lipsticks from 19 manufacturers in the USA [12]. Extraction of metals, among them cadmium, in this research, was done with mixture of concentrated HNO₃: HF (3:1) and with addition of conc. HCl, which is more aggressive method of extraction than both methods applied in our work. Similar low levels of cadmium in lipsticks as in this work was also found in the lipsticks taken from the markets in Kano Metropolis in Nigeria, with concentration range of 0,07-1,67 mg Cd/kg and extraction from the ashed samples with HNO₃ solution, c=1mol/L [13]. On the contrary, higher contents of cadmium were found in lipsticks in Iran. Nourmourdi et al. have analyzed 35 samples of lipsticks and found the cadmium level from 4,08-60,20 mg/kg by the extraction with concentrated HNO₃ and H₂O₂ [14].

Table 1. Content of Cd in the investigated cosmetic products

Sample number	Cosmetic product	Brand	Shade	Production country	Cd (mg/kg)	
					0,1M HCl	Aqua Regia
1.	lipstick	Max Factor	red	Ireland	<0,01	<0,01
2.	lipstick	Art Deco	red	Germany	<0,01	<0,01
3.	lipstick	Rimmel	dark red	England	<0,01	<0,01
4.	lipstick	Bourjois	red	Italy	<0,01	0,26
5.	lipstick	Catrice	coral red	Germany	0,05	0,17
6.	eyeshadow	Rimmel	green	England	<0,01	0,09
7.	eyeshadow	Catrice	gold	Germany	<0,01	0,11
8.	eyeshadow	Essence	smooth caramel	Germany	0,14	0,26
9.	eyeshadow	Revelique	purple	Austria	<0,01	<0,01
10.	eyeshadow	Catrice	black	Germany	<0,01	<0,01
11.	blush	Art Deco	brown orange	Germany	<0,01	<0,01
12.	blush	Maybelline	rose	Italy	0,10	0,22
13.	blush	Essence	purple rose	Germany	<0,01	<0,01
14.	blush	Misslyn	peach	Germany	<0,01	<0,01
15.	blush	Rimmel	rose	England	<0,01	0,25

In analyzed eyeshadows from the market in the Republic of Srpska, low concentrations of Cd (Table 1) were found. In some of the analyzed samples after extraction with aqua regia, slightly higher concentrations of Cd were found than in diluted HCl extracts (samples number 6,7 and 8). None of the analyzed samples of the eyeshadows exceeded the permitted values (5 mg Cd/kg) according to our regulations [10]. Similar low level of cadmium, with mean of 0,032 mg Cd/kg, was found in eyeshadows in study done in USA [12]. Through analysis of the 15 eyeshadow samples in Iran Nourmoradi et al. [14] found cadmium content between 1,54-55,59 mg/kg,

what is higher than level of cadmium found in the same cosmetics in this work.

The contents of cadmium in the investigated blushes were mainly lower than 0,01 mg/kg (Table 1), with exception of the samples number 11 and 15. Analysis of the sample number 11 resulted by 0,1 mg Cd/kg in diluted HCl extract and 0,22 mg Cd/kg in aqua regia extract. On the other side, the aqua regia extract of the sample number 15 contented 0,25 mg Cd/kg. Comparing the determined concentrations by maximum permitted level (5 mg Cd/kg) in our regulations [10], it has been found that all analyzed samples were correct and safe. Analysis

of the cadmium content in the blushes in the USA showed low level of cadmium as well as for the analyzed blushes in this study. During the analysis of the 30 blushes from 20 manufacturers, Hepp et al. found that the mean value of the cadmium content was 0,056 mg/kg [12]. Similar low level of cadmium (less than 0,3 mg/kg) in the examined blushes was also found in cosmetic stores within Kaduna Metropolis in Nigeria [15].

4. CONCLUSIONS

Heavy metals are present in cosmetic products as the impurities from the raw material. Following such observation, there is increasing need to investigate the concentration of cadmium just as well as other toxic elements (e.g. As, Pb, Hg) in some commonly used cosmetic products. It has been found a low level of cadmium in the investigated cosmetic products (lipsticks, eyeshadows, blushes) presented in the market in the Republic of Srpska.

This work showed that determined cadmium contents in the analyzed samples of lipsticks, eyeshadows and blushes were below the maximum permitted levels defined by our regulations [10] and therefore these products are safe and healthy according to cadmium content.

In spite of the fact that the cadmium contents were mainly in trace amounts, because of toxicity of this element and frequent, repeated application of the cosmetic onto the skin, consumers must be aware of the possible risk. Also, because of the tendency of cadmium and other toxic elements to accumulate in the human body, it is important to continuously control (monitor) the quality of the cosmetic products according to the concentrations of these elements.

5. ACKNOWLEDGEMENT

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ПРОЦЕНА САДРЖАЈА КАДМИЈУМА У КОЗМЕТИЦИ МЕТОДОМ ЕКСТРАКЦИЈЕ ПОМОЋУ РАЗБЛАЖЕНЕ HCl И ЦАРСКЕ ВОДЕ

Сажетак: Интензиван индустријски и технолошки развој резултовао је ослобађањем значајних количина штетних материја и токсичних супстанци у биосферу, међу којима значајан удио имају тешки метали. Поједини тешки метали су биогени (Cu, Zn, Se, итд.) и неопходни за одржавање метаболизма у људском тијелу. Главне пријетње људском здрављу су повезане са излагањем токсичним елементима, као што су Pb, Cd, Hg и As. Емисија Cd у животну средину је порасла током 20. вијека, посебно захваљујући томе што се производи који садрже кадмијум могу рециклирати. Cd има кумулативно дејство са билошким полуживотом у организму од 10 до 30 година и може изазвати значајне токсичне ефекте. Козметички производи су потенцијалан извор Cd и других тешких метала, нарочито због честе и неконтролисане употребе разних козметичких препарата лошег и/или сумњивог квалитета. Циљ овог рада је био да се одреди садржај Cd у различитим козметичким производима (ружеви за усне, сјене за очи и руменила) присутним на тржишту Републике Српске. Садржај Cd је одређен методом атомске апсорпционе спектрофотометрије (ААС) након екстракције са разблаженом HCl и царском водом. Резултати истраживања указују на то да су концентрације Cd у испитиваним производима у складу са прописима Републике Српске (Правилник о безбједности предмета широке потрошње, Службени гласник Републике Српске – бр.17/15).

Кључне ријечи: кадмијум, козметика, атомска апсорпциона спектрофотометрија, законска регулатива.

