Macedonian pharmaceutical bulletin, **70** (2) 41 - 46 (2024)
ISSN: 1857-8969
DOI: 10.33320/maced.pharm.bull.2024.70.02.006
Professional paper

ICP-OES analysis of heavy metals in cosmetic products on the Macedonian market

Marina Denkovska[1*], Viktorija Duridanska[1], Tatjana Kadifkova Panovska[2]

[1]*Center for Public Health Skopje, III Macedonian Brigade 18, 1000 Skopje, North Macedonia*
[2]*Institute of Applied Biochemistry, Faculty of Pharmacy,*
Ss. Cyril and Methodius University in Skopje, Mother Theresa 47, 1000 Skopje, R. North Macedonia

Received: November 2024; Accepted: February 2025

Abstract

The aim of this research was to determine concentration of lead (Pb), cadmium (Cd), chromium (Cr), and nickel (Ni) in selected cosmetic products available on the Macedonian market. The sample preparation procedure consisted of acid digestion followed by evaporation to dryness and dissolving the dry residue with 2% HNO_3 for further analysis. Heavy metal content was determined utilizing Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). Lead was found in 18 of the analyzed samples and its concentration ranged 0.07 to 1.23 mg/kg. Cadmium was found in 14 samples and its concentration ranged 0.05 to 0.10 mg/kg. Chromium was found in 13 of the samples and its concentration ranged 0.07 to 3.25 mg/kg. Nickel was found in 8 of the samples and its concentration ranged 0.07 to 2.58 mg/kg. The obtained results from the study show that heavy metal levels in the selected cosmetic products were within the permissible levels according to the Macedonian legislation. However, given the toxic effects these substances exert on a long term basis, their content in cosmetic products, should be continuously monitored in order to assure lowest risks as well as safe application of these products.

Key words: cosmetic products, heavy metals, quality control, public health

Introduction

Cosmetic products can be defined mixtures of different ingredients intended to be placed in contact with the external parts of the human body (epidermis, system, nails, lips and external genital organs) or with the teeth and the mucous membranes of the oral cavity (European Regulation EC No 1223/2009). They are intended for cleaning, perfuming, changing the appearance, protection, or correction of body odors. As self-care and well-being become increasingly important for consumers worldwide, the cosmetic industry becomes influential, and trends indicate that this industry will continue to expand (Đogo-Mracevic et al., 2023).

Cosmetic products can contain different contaminants. Some contaminants are present as a result of the chemical synthesis process of the cosmetic ingredient, some are unintentionally included in the product (chemical contaminants) and depending on the type of the product, microbial contamination can be present. One group of contaminants that attracts special attention nowadays are the metal contaminants. They can be found in a range of cosmetic products, including eye shadow, whitening toothpaste, nail polish, sunscreen, foundation, lipstick, and hair colors. Additionally, heavy metals that pollute the natural environment are absorbed by plants and may exist in seed oils and other parts of the plants that are to be used as raw materials of cosmetics products (Hussein, 2015; Ruiz et al., 2019; Zakaria and Ho, 2015). Other metals

*email: marina_vidanovska@hotmail.com

serve as additives or colorants because of their specific properties. For example, chromium (III) is used in a very small number of products as a colorant, and iron oxides are common colorants in eye shadows and blushes. Also, some color additives may be contaminated by heavy metals. Annex II of the Cosmetics Regulation (EC) No 1223/2009 lists the heavy metals and their derivatives that are prohibited, while Annexes III, IV, V, and VI list the metals that can be used at a maximum concentration in the cosmetic products (EC 1223/2009). Heavy metals, as a subgroup of the metal contaminants, includes elements such as mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Tl), nickel (Ni), and lead (Pb) which can be highly dangerous for human health and the environment. The interest in heavy metal levels in the cosmetic industry is of crucial importance for several reasons, as stated by various authors: human health, vulnerable populations, cumulative exposure, consumer trust, regulatory compliance, environmental impact, long-term consequences, global trade, representation and awareness, and ethical responsibility (Chauhan et al., 2010; Saeed et al., 2010).

The European law for cosmetic as described by the EU council states that all cosmetics in human use must be completely harmless for users and the final liability to ensure the safety of these preparations lies on the manufacturers, distributors as well as on importers. The European Commission on Health and Food Safety provides a catalog of substances that must be restricted in cosmetic products. Unluckily, in many cases the use of cosmetics is related to the occurrence of un-favorable effects that are due to the existence of toxic chemical substances in their preparations. It has been reported that presently in many accessible cosmetic products around 10,000 chemical substances and various metals are present. The existence of toxic heavy metals such as lead, chromium and nickel, above the safe permissible limits in everyday use of beauty products and cosmetics is of great concern. Such toxic metals are commonly used in almost all of the cosmetics like eyeliner, lipsticks, toothpaste, and henna etc. Particularly, the Pb and Cr are generally used in cosmetics as a source of pigmentation and Ni is aimed as a source of improving the beautification.

The control and monitoring the cosmetic product quality are significant practices that guarantee that cosmetics preparations are safe and effective (Alam et al., 2019; Arshad et al., 2020). A desired quality in the finished product is granted when the quality is controlled and maintained in each step from acquiring the raw material until the product reaches the consumer. As different cosmetic products are continuously produced and introduced into the market, quality concerns have increased (Akhtar et al., 2022).

Saeed and collaborators confirm that regulation is necessary because many cosmetic product labels typically do not specify the specific heavy metals present in the product; they only list the main ingredients while contaminants remain undisclosed (Saeed et al., 2010).

Increased exposure to heavy metals present in cosmetic products may result in numerous adverse health effects including skin allergies, oxidative stress, neurotoxicity, memory loss, adverse effects on the reproductive system or carcinogenic health effects (Arshad et al., 2020). Therefore, the aim of this study was to determine the concentration of selected heavy metals (Pb, Cd, Cr, and Ni) in cosmetic products utilizing Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES).

Material and methods

Sample collection

For the study, 35 cosmetic samples from different popular cosmetic brands were purchased from local markets and beauty shops in Skopje, Republic of North Macedonia. The selected products were of different qualities and price ranges, mostly facial creams and baby's creams, face masks, ointments and tooth pastes. To keep the brand names anonymous, products were coded. Samples were stored at room temperature until analysis. Samples and their respective codes, as well as other details for the investigated products are presented in Table 1.

Chemicals and reagents

All the chemicals and reagents were of analytical extra pure grade. HNO_3 (65%, Fisher Chemical), HCl (37%, Carlo Erba SAS) and water of electrical conductivity (0.055 μS), suitable for working with the ICP-OES apparatus, were used for digestion and dilution of samples as well for preparation of blank and standard solutions. Multi-element ICP standard solution containing 24 elements (100 mg/L) was obtained from Carl Roth, Germany. Standard solutions for the calibration curves of all investigated heavy metals were prepared in the concentration range 0.05-5.0 mg/L.

Sample preparation and analysis

Sample preparation for determination of lead, cadmium, chromium and nickel in facial and baby's creams, face masks, ointments and tooth pastes was conducted according to official method given in the "Regulation on methods for determining toxic metals in articles for general use and cosmetic products" (Official Gazette 46/83, 1983). The investigated heavy (toxic) metals were extracted using the following procedure: 5g of each tested sample was weighed and placed into 250 mL ground Erlenmeyer flask. The next step consisted of addition of 75 mL 37% HCl and the flask containing the sample was placed on a reflux condenser to boil for 15 minutes (solution 1). After removing the flask from the condenser, the sample was cooled down, the obtained solution was filtered through filter paper into a 100 mL

Table 1. Samples, their respective codes and details about the investigated samples

Cosmetic product type	Product code	Other characteristics	Country of origin
Creams			
	C1	Facial cream	Slovenia
	C2	Soft cream	Germany
	C3	Strech marks cream	R. Macedonia
	C4	Day cream	R. Macedonia
	C5	Baby cream	R. Macedonia
	C6	Universal cream	Bulgaria
	C7	Goat's milk hand cream	Poland
	C8	Honey /vit. C face cream	Poland
	C9	Night crème with hyalurone	Germany
	C10	Skin cream	R. Macedonia
	C11	Baby cream	R. Macedonia
	C12	Bio cream	France
	C13	Face cream	Norway
	C14	Face cream	Germany
	C15	Hand crème	Czech Republic
	C16	Antipigment cream	Germany
	C17	Body and face cream	France
	C18	Hydration cream	UK
	C19	Anti-aging face cream	Germany
	C20	Face cream	France
	C21	Face cream	France
	C22	Face cream	France
	C23	Hand cream	Bulgaria
	C24	Hand cream	Italy
Ointments			
	O1	Ointment	R. Macedonia
	O2	Baby ointment	Serbia
Face masks			
	M1	face mask in pregnancy	R. Macedonia
	M2	face mask rich in antioxidants	R. Macedonia
	M3	nourishing face mask	R. Macedonia
	M4	anti-acne face mask	R. Macedonia
	M5	anti-acne face mask	R. Macedonia
	M6	face moisturizer	Germany
Tooth pastes			
	T1	contains cooling crystals	Switzerland
	T2	children's tooth paste	UK
	T3	children's tooth paste	UK

Table 2. Optimal operational/instrumental parameters

Parameter	Optimal value
Radio Frequency Power	1500 W
Radio Frequency matching	50 Hz
Nebulizer gas flow	0.70 L/min
Plasma gas flow	10 L/min
Auxiliary gas flow	0.2 L/min
Nebulizer pump	1.5 mL/min
Spray chamber temperature	38 °C

flask. The Erlenmeyer flask was thoroughly rinsed with small amount of distilled, lukewarm water and this liquid was added to the 100 mL flask. The volume was made up to the mark using the 37% HCl (solution 2). Solution 2 was quantitatively transferred to a 250 mL beaker, evaporated to dryness, dissolved with 2% HNO_3 and then quantitatively and transferred into a 100 mL flask for further analysis.

ICP-OES, model Perkin Elmer Avio 200 was used for the heavy metal determination in the investigated cosmetic samples. After igniting the plasma, the instrument was heated up for 30 min. Optimal operational/instrumental parameters are shown in Table 2. The concentration of the above mentioned heavy metals was calculated from the calibration curve and the results were reported as mg/kg. The glass volumetric flasks and/or plastic were soaked in 6% HNO_3 for 24 hours, rinsed with deionized water and dried. An axial plasma view was selected for Ni (231.604 nm), Cd (228.802 nm), Pb (220.353 nm) and Cr (267.716 nm).

Results and discussion

In our study, levels of Pb, Cd, Cr, and Ni, in selected cosmetic products were determined using ICP-OES. The concentration ranges of the examined elements in creams, ointments, face masks and the toothpastes is presented in Table 3.

Cr, Ni and Cd belong to the category of carcinogenic metals according to the International Agency for Research on Cancer (Zhu and Costa, 2020). The primary route these metals enter the human body from cosmetic is through dermal absorption. They accumulate in the human organism, disrupt different cellular functions and mechanisms, thus increasing the risk of cancer-related diseases due to oxidative stress, DNA damage and cell death (Ahmed et al., 2024; Massadeh et al., 2017).

The results shown in Table 3 imply that heavy metal levels in all the tested samples were within maximal permissible concentrations. In our study, lead was detected in 18 of the tested products but the obtained levels were far below the maximum permitted concentrations. The obtained values for lead concentrations ranged 0.07-1.23 mg/kg**.** The highest Pb concentration measured was 1.23 mg/kg, but this value was far below the MPC. The only products where lead was not detected were the facial masks examined. According to Article 105 of the Regulation on the conditions regarding the health safety of products for general use and cosmetics that can be placed on the market (Official Gazette 46/83, 1983), eye care and eye coloring products, product that remain on the skin for a longer period, lip care and coloring products as well as oral care products must not release more than 30 mg of lead, 20 mg of lead and 10 mg of lead, respectively (the above values are calculated as per 1 kg of product).

Pb in cosmetic products poses significant risks to human health. It is a heavy metal that builds up in the body over time and causes a number of harmful health effects. Pb exposure from cosmetics has been connected to developmental delays, cancer, neurological impairment, and reproductive complications. Pb-containing cosmetics are particularly concerning for pregnant women as lead exposure during pregnancy can harm the developing fetus. The FDA, EU, GCC, ASEAN, China, Canada, and Korea have guidelines to limit Pb (20 for colorant used in cosmetics, 10 for lip cosmetics) to 2.0, 10, 20, 10, and 20 mg/kg, respectively (Ahmed et al., 2024; Attard, 2022; Halicz et al., 2015).

Table 3. Concentration ranges for Pb, Cd, Cr, and Ni (mg/kg) in the examined cosmetic products from the Macedonian market

Product/respective codes	Heavy metal levels (mg/кg)			
	Pb	Cd	Cr	Ni
Creams (C1-C24)	0.07-1.23	0.05-0.10	0.07-3.25	0.07-2.58
Ointments (O1-O2)	0.20-0.62	ND	ND	NA
Facial masks (M1-M5)	ND*	ND	NA	ND
Tooth pastes (T1-T3)	0.06-1.20	ND	ND	NA**
MPC **	30	5	50	50
EU regulative	0.5	0.5	1	NA
WHO	10	0.3	NA	NA
Scientic Committee on Consumer Safety (SCCS)	20	5	NA	200

*ND-not detected; NA- not applicable

**MPC according to the Regulation on the conditions regarding the health safety of items for general use that can be placed on the market (Службен весник 26/83)

Cd is a toxic heavy metal that can be found in various cosmetic products. Exposure to Cd through cosmetics can lead to severe health effects, including stomach irritation, vomiting, and diarrhea, and long-term exposure may result in kidney, liver, and brain damage. Therefore, it is crucial that regulatory authorities monitor and regulate the levels of cadmium in cosmetics to ensure consumer safety. The EU, GCC, ASEAN, China, Canada, and Korea have guidelines to limit Cd to 0.1, 3, 5, 5, 3 and 5 mg/kg, respectively (Ahmed et al., 2024; Attard, 2022; Halicz et al., 2015).

In our study cadmium was determined only in facial cream samples and the ointment samples whereas no cadmium was measured in the samples belonging to the facial masks and the tooth pastes. The Cd levels ranged 0.05-0.23 mg/kg (Table 3). The obtained results were within the maximal permissible concentrations.

The Cr concentrations in the investigated samples ranged 0.07-3.25 mg/kg for the analyzed facial creams and 0.05-0.08 mg/kg in the examined facial masks. No Cr was detected in the ointments and the tooth pastes.

Cr in its hexavalent form is more toxic than its trivalent form. Although Cr (VI) is not legally restricted as an ingredient in cosmetics, its presence must be controlled as an impurity due to its harmful effects on human health. Certain Cr-containing compounds, with long-term exposure, can present health hazards. Cr (III) is comparatively stable, has low water solubility, and is essential in small amounts for human health. Conversely, chromium (VI) is highly toxic, mobile, and soluble in water. It is utilized in various industrial processes, which can result in human exposure, including cosmetics. The FDA does not have a specific limit for Cr in cosmetics. However, it restricts Cr levels as an impurity in some approved color additives to 50 mg/kg. The EU has a stricter limit. Cr is allowed in cosmetics, but only up to a maximum of 1 mg/kg of the product (Halicz et al., 2015).

The presence of nickel in cosmetic products can lead to headache, sleeplessness, nausea, vomiting, dizziness, and disruption in cell membrane metabolism. The most common manifestations include allergic contact dermatitis and Ni allergy syndrome as well as occurrence of teratocarcinoma type of cancer. It is also worth mentioning that the safe permissible limit of Ni as recommended by EPA authorities is 1.00 ppm in cosmetics. Ni can be found in a variety of cosmetic products, mostly as a trace element in colorants and preservatives, or as a contaminant in raw materials and pigments. It is present in cosmetics such as hair dyes, lipsticks, and eye makeup. Notably, the first documented instance of Ni allergy attributed to eye shadow has been reported, with sensitivities triggered even at minute Ni concentrations, potentially exacerbating pre-existing allergies. Vigilance regarding Ni exposure and its associated health risks is paramount, necessitating stringent regulation and monitoring measures. Within the EU, Ni and its salts are prohibited in any cosmetic product. The permissible limit for Ni in cosmetics is set at 10 mg/kg according to global standards (Attard et al., 2022; Halicz et al., 2015). In our study, Ni was measured only in the group of facial creams, with concentrations ranging from 0.07-2.58 mg/kg (Table 3).

Conclusion

In this study, the concentration of Pb, Cd, Cr, and Ni in cosmetic products was examined using ICP-OES. The obtained results were within the MPCs for the studied metals according to the Macedonian laws. The examined products can be considered safe according to current cosmetic regulations in different part of the world. The data obtained from this study can be used by everyone interested in safety of cosmetic products available on the market. Also, continued research is essential to better understand the extent of exposure and its long-term health implications, ultimately informing regulatory policies and consumer choices towards safer cosmetic products. In general, the conclusion is that continuous awareness, proper regulation, consumer awareness, and industry responsibility are crucial to ensuring that cosmetic products are safe for use and do not pose unnecessary health risks due to heavy metal contamination.

References

European Regulation EC No 1223/2009

Akhtar, A., Kazi, T.G., Afridi, H.I., Khan, M., 2022. Human exposure to toxic elements through facial cosmetic products: Dermal risk assessment. Regul. Toxicol. Pharmacol. 131, 105145.

Alam, M.F., Akhter, M., Mazumder, B., 2019. Assessment of some heavy metals in selected cosmetics commonly used in Bangladesh and human health risk. J. Anal. Sci. Technol. 10, 2. https://doi.org/10.1186/s40543-018-0162-0

Al-Saleh, I., Al-Enazi, S., Shinwari, N., 2009. Assessment of lead in cosmetic products. Regul. Toxicol. Pharmacol. 54, 105–113.

Arshad, H., Mehmood, M.Z., Shah, M.H., Abbasi, A.M., 2020. Evaluation of heavy metals in cosmetic products and their health risk assessment. Saudi Pharm J. 28(7), 779-790. https://doi.org/10.1016/j.jsps.2020.05.006

Attard, T., Attard, E., 2022. Heavy metals in cosmetics. In Environmental Impact and Remediation of Heavy Metals; IntechOpen Limited: London, UK.

Chauhan, A.S., Bhadauria, R., Singh, A.K., Lodhi, S.S., Chaturvedi, D.K., Tomari, V.S., 2010. Determination of lead and cadmium in cosmetics products. J. Chem. Pharm. Res. 2, 92-97.

Đogo Mracevic, S., 2023a. Cosmetics market size & Share Report 2030 / The Brainy Insights;

Djogo-Mracevic, S., Laketić, T., Stanković, M., 2023b. Toxic element determination in selected cosmetic products: health risk assessment. Environ. Monit. Assess. 195. https://doi.org/10.1007/s10661-023-11664-1

Halicz, L., Portugal-Cohen, M., Russo, M.Z., Robino, F., Vanhaecke, T., Rogiers, V., 2015. Safety evaluation of traces of nickel and chrome in cosmetics: The case of Dead Sea mud. Regul. Toxicol. Pharmacol. 73, 797–801.

Hussein, H.J., 2015. Evaluation of the concentration of some heavy metals in hair dyes in Baghdad. Int. J Sci. Res. 4(2), 687-691.

Jokanović, M. ,2001. Toksikologija. Elit Medika, Beograd.

Massadeh, A.M., 2017. Evaluation of Cd, Cr, Cu, Ni, and Pb in selected cosmetic products from Jordanian, Sudanese, and Syrian markets

Moerr, 2016. Тешки метали, available at: https://air.moepp.gov.mk/?page_id=164

Ruiz, L.R., Ortiz, L.D.R.V., de Oliveira, T.S.B., da Rosa Maluf, A.P.B., Buchala, C.A., Fernandes, P.G., Tempest, L.M. and Zotarelli Filho, I.J., 2019. Investigation of the presence of heavy metals and other contaminants in labor cosmetics and their health risks in general. Health Science Journal, 13(3), .1-3.

Saeed, M., Muhammad, N., Khan, H., Khan, S.A., 2010. Analysis of toxic heavy metals in branded Pakistani herbal products. J. Chem. Soc. Pak. 32, 471-475.

SCCS, 2012. The SCCS's notes of Guidance for testing of cosmetics substances and their safety evaluations 8th revision-adopted at its 17th plenary meeting of 11 December 2012 (SCCS/150112).

Tarone, R.E., 2018. On the International Agency for Research on Cancer classification of glyphosate as a probable human carcinogen. Eur. J. Cancer Prev. 27, 82–87. https://doi.org/10.1097/CEJ.0000000000000289

Zakaria, A. and Ho, Y.B., 2015. Heavy metals contamination in lipsticks and their associated health risks to lipstick consumers. Regulatory toxicology and pharmacology 73(1), 191-195.

Службен весник на РМ, 2007. Закон за безбедност на козметичките производи, бр.55.

Службен весник 26/83, 1983. Правилник за условите за здравствена безбедност на предметите за општа употреба што може да се пуштат во промет.

Резиме

ICP-OES анализа на тешки метали во козметички производи на пазарот во С. Македонија

Марина Денковска[1*], Викторија Дуриданска[1], Татјана Кадифкова Пановска[2]

[11]Центар за јавно здравје Скопје, III Македонска Бригада 18, 1000 Скопје, С. Македонија
[2]Институт за применета биохемија, Фармацевтски факултет, Универзитет „Св. Кирил и Методиј", Мајка Тереза 47, 1000 Скопје, С. Македонија

Клучни зборови: козметички производи, тешки метали, контрола на квалитет, јавно здравје

Целта на нашето истражување беше определување на концентрацијата на олово (Pb), кадмиум (Cd), хром (Cr) и никел (Ni) во определени козметички производи достапни на пазарот во Република Северна Македонија. Подготовката на примероците се состоеше од дигестија во киселина по што беа упарени до суво, а сувиот остаток беше растворен во 2% HNO_3 за понатамошна анализа. Содржината на испитуваните тешки метали беше определена со примена на индуктивно спрегната плазма оптичка емисиона спектрометрија (ICP-OES). Олово беше најдено во 18 примероци и неговата содржина се движеше од 0,07 до 1,23 mg/kg. Кадмиум беше определен во 14 примероци и неговата содржина се движеше 0,05 до 0,10 mg/kg. Хромот беше определен во 13 примероци, во концентрации 0,07 до 3,25 mg/kg. Никелот беше определен во 8 од испитуваните примероци, во концентрации од 0,03 до 2,58 mg/kg. Имајќи ги предвид токсичните ефекти што настануваат како резултат на хронична изложеност, концентрацијата на тешки метали во козметички производи треба постојано да се следи со цел да се намали ризикот од токсични ефекти и да се овозможи безбедна употреба на козметичките производи.