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Toxicological analytical methods for metals identification in cosmetics

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ABSTRACT
BACKGROUND: Cosmetic Toxicology involves the study of substances contained in beauty products that can accumulate in the body such as lead (Pb), aluminum (Al), cadmium (Cd), nickel (Ni), mercury (Hg), chromium (Cr), copper (Cu), zinc (Zn), iron (Fe). These substances reach tissues and the bloodstream and can cause long-term damage such as hormonal disorders and carcinogenic events. OBJECTIVES: To evaluate the toxicological analytical methods commonly used in the identification and/or quantification of heavy metal cosmetic ingredients. METHODS: A literature review was conducted with a targeted search of scientific articles during the month of June 2019 in the PubMed and Scielo databases published between 2009 and 2019, using the keywords: toxicology, cosmetic, metal. RESULTS: Spectrometry is the most widely used toxicological method in the detection of heavy metals in cosmetics and presents good accuracy and reliability. In the analyzed studies, several spectrometry variations were used, such as Atomic Absorption Spectroscopy, Inductively Coupled Plasma Atomic Emission Spectrometry, Optical Emission Spectrometry. Among the products analyzed for metals, lipstick was the most prevalent cosmetic (in 69% of cases), followed by eye shadows (in 38.4% of articles). CONCLUSIONS: The presence of heavy metals such as Pb, Al, Cr, Cd seems to be widely present in cosmetics such as lipsticks and eye shadows, at levels above the considerable safe.

Keywords: Cosmetic, Metals, Toxicology, Method.

1 INTRODUCTION

Toxicology refers to the study of exposure to chemicals as well as the adverse effects resulting from this interaction (HAYES et al., 2017). Toxic agents are those originating from heavy metals such as aluminum, cadmium, lead, arsenic, mercury which can accumulate causing deleterious effects in the long term (NORDBERG et al., 2007). The study of toxicology includes food, occupational, social, environmental, drug and cosmetic toxicology, the latter of which has gained prominence in the last 20 years given the increase of 4.5% in the production of cosmetics in the world per year (FISCHER et al., 2017). In addition, cosmetic toxicology is related to environmental toxicology (plants used in the production of products may be contaminated with heavy metals) and social toxicology (cosmetics are absorbed by individuals through the skin or ingestion) (BOCCA et al., 2014).

It is estimated that an adult uses, on average, nine types of cosmetics per day, exposing themselves to more than 120 chemicals that can accumulate in the body and even cause disease (*Environmental Working Group-EWG)*. Examples of cosmetics that may include harmful substances include antiperspirants (containing aluminum), makeup (containing lead), toothpaste (containing fluoride), henna capillary (containing ammonia), creams and lotions (containing aluminum, lead). Also, additives that give color to cosmetics can be contaminated by metals such as Pb and Hg (EWG, 2007). These products should, in theory, be inert and not cause harm to health, however the intentional or accidental presence of chemicals is unfortunately a reality in cosmetics (BOROWSKA et al., 2015).

Toxic metals present in cosmetics can be retained in the tissues, acting directly on the skin or be absorbed reaching the bloodstream, accumulate in the body, exerting toxic effects and reaching organs (BOCCA et al., 2014). In addition, topical effects such as allergic and systemic contact dermatitis may occur due to exposure to metals present in cosmetics (FILON et al., 2009). Some of the long-term effects of metal damage include increased risk of cancer, reproductive problems and development of neurological disorders, cardiovascular, kidney and kidney problems, contact dermatitis and hair loss (LIU et al., 2013). Data from Pineau et al. (2014) indicate that the aluminum present in antiperspirants presents a health risk and should be reduced. The authors indicate a strong relationship of this metal with carcinogenesis and the development of breast cancer based on evidence of accumulation of the metal in the mammary gland. Also, preservatives like parabens are harmful given their interference with the hormonal system, increasing the risk of hormonal disorders like obesity, infertility, thyroid, breast cancer (NOWAK et al., 2018).

In view of the potential toxicity of cosmetics and their adverse effects on organisms and the environment, it is of paramount importance that there is control over the presence and concentration of heavy metals in these products. Therefore, the aim of the present study was to evaluate the toxicological analytical methods commonly used in the identification and/or quantification of heavy metal cosmetic ingredients.

2 MATERIALS AND METHODS

The present study is a literature review on the toxicological analysis techniques used in the detection of substances in cosmetic products. The review consisted of the targeted search of scientific articles during the month of June 2019 based on the PubMed and Scielo databases and published between the years 2009 to 2019, using the keywords: *toxicology, cosmetic, metal.* The results of the bibliographic survey were tabulated and described in a table to exemplify the techniques employed, elements analyzed, as well as to discuss the results.

3 RESULTS AND DISCUSSION

In view of the potential toxicity resulting from the repeated and progressive use of cosmetics, the present work sought to observe the toxicological analytical methods employed in the detection of heavy metals in these products, through a scientific literature review. The search results in the PubMed and Scielo databases (presented in Table 1) were satisfactory and totaled 13 studies that directly contemplated the theme. A study by Atz and Pozebom (2009) performed the toxicological detection of metals in cosmetics such as eye shadow and lipstick, using the methods Graphite Furnace Atomic Absorption Spectrometry (GFAAS) and Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-OES). The authors observed the presence of the trace elements Cr (1.29%), Ni (106 µg/g-1) and Cu (9.90%), and the concentrations investigated in lipstick were below those found in eye shadows, probably due to the basic matrix of lipstick composed of waxes and oils - where inorganic oxides are present in lower concentrations.

Among the articles surveyed, lipstick was the most prevalent cosmetic (in 69% of cases), followed by eye shadows (in 38.4% of articles), because, according to Orisakwe (2013), these items are more "dangerous" due to their greater absorption and ingestion given the proximity of the mucous membranes. The same author conducted a study in Nigeria to assess the levels of metals Pb, Cd, Ni, Cr, Hg in lipsticks and other cosmetics and noted that the detected levels of lead and cadmium were higher than the permissible limits in water and food (15 ppb and 5 ppb – parts per billion, respectively). In addition, based on the dermal toxicity study in albino rats by Tsankov et al. (1982) where the maximum permissible concentration of lead should be ≈10 ppm (parts per million) only 2 (4%) of the 50 cosmetics tested by Orisakwe (2013) showed the appropriate level of lead (>10ppm).

Study conducted in Jordan, evaluated the levels of metals as Pb, Cd, Ni, Al in lipsticks, eye liner, mascara, facial base and observed high levels of these constituents in the products. According to the authors, Pb was detected in all eye shadow samples evaluated with concentrations up to 153.89 ± 17.03 ppm (when the ideal would be up to 15 ppb) (FARRAD et al., 2015). In addition, the Ni concentration was detected in the eye shadow up to 31,909 ± 3.34 ppm being a factor for increased allergic eye infection and important cause of eczema on the hands (ORISAKWE et al 2013). The permissible limits of Pb, Cd, Cr for water and food are 15, 5 and 100 ppb (GONDAL et al 2010), evidencing that concentration for these elements in this study is much higher than the allowed limits. Therefore, according to Farrad (2015), the daily and continuous use of these cosmetics can result in the accumulation of metal levels in the human body above the permissible limits, causing harmful effects to individuals in the long term.

Data from Liu (2013) demonstrated the presence of lead in 75% of the products analyzed, with an average concentration of up to 1.32 ppm (within acceptable). However, even some items presenting individually acceptable levels of metals, the author argues that when added 10 products tested, the acceptable daily dose of metals would be far beyond the ideal - indicating the harmful effect of the accumulation of products. Also, a study by Gondal (2010) showed that the concentration of several toxic carcinogenic contaminants (lead, chromium, cadmium and zinc) were present in lipstick samples in Saudi Arabia with levels above the permissible safety limits, which is a cause of great concern.

According to Liu (2013) the level where there is no observed adverse effect (NOAEL) for Pb is 2.86 µg/day, Al is 125 mg/day, Cd is 19 µg/day, Ni is 1.12 mg/kg-day and Cu is 426 µg/kg-day, but the cumulative effect of ingestion and exposure to these compounds can be very harmful. For example, Cd and its compounds are considered carcinogenic to humans and their inhalation exposure is associated with lung cancer and chronic oral exposure to kidney and bone damage, according to Liu (2013).

In addition, animal studies indicate that young animals may absorb more Cd than adults and be more susceptible to bone deficiencies (OGOSHI et al. 1989) and feeding rats and mice with high Cd levels (1 to 20 mg/kg/day) has demonstrated low birth weight and behavior and learning problems (Agency for Toxic Substances and Disease Registry/USA, 2008). Heavy metals can also arise during the production chain process. For example, various ingredients derived from non-organic plant sources, such as cottonseed oils and rice derivatives, may contain metals such as Pb and Hg (EWG, 2007). Also, Co Cr and Ni, are potent skin sensitizers to cause dermatitis, while As, Cd, Hg, Pb and Sb are highly toxic with many long-term effects (THYSSEN, 2010).

TABLE 1. List of studies involving toxicological analysis of metals in cosmetics, searched in the PubMed and Scielo databases between 2009 and 2019.

Method	Substances analysed	Cosmetic product analyzed	Reference
Graphite Furnace Atomic Absorption Spectrometry (GFAAS) Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-OES)	As, Cd, Co, Cr, Cu, Ni, Pb	Eye shadow Lipstick	Atz, Pozebon. 2009.
inductively coupled plasma mass spectrometry (ICP-MS)	Pb	Lipstick	Hepp et al., 2012
Atomic Absorption Spectrophotometer	Pb, Cd	Lipstick	Nkansah et al. 2018.
Flame emission spectrophotometer	Pb, Cd	Lipstick	Ziarati et al., 2012.
Parent-Indutious Plasma Mass Spectrometry (ICP-MS)	Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Zn, Sb, Se	lipstick, eyeliner, henna, eyeshadows, cream, moisturizers and facial powder.	Al-Qutob et al., 2013.
Parent-Indutious Plasma Mass Spectrometry (ICP-MS) Plasma-coupled atomic emission spectrometry (ICP-AES)	Ag, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sn, Sr, Ti, Tl, U, Zn, Zr, Nb, Rb, Sb, Se	lipstick, eyeliner, eye shadows, mascara.	EMAD et al., 2015.

Electrothermal Atomic Absorption Spectrometry Inductively Coupled Plasma Optical emission spectrometry Flame Atomic Absorption Spectrometry Cold Steam Atomic Absorption Spectrometry	As, Cd, Cr, Cu, Hg, Mg, Mn, Ni, Sr and Zn	Shampoo, hair gel, body milk, Hair conditioner and body oil	Lavilla et al., 2009
Plasma-coupled atomic emission spectrometry (ICP-AES) and ICP-MS	Ni, Cr	Dead Sea Mud (cosmetic ingredient)	Ma'or et al., 2015
Atomic absorption spectroscopy	Pb, Cd, Hg	Plants used in cosmetics	Fischer et al., 2017
Atomic Absorption Spectrometer	Pb, Cd, Ni, Cr, Hg	Creams, lotions, facial powders, soaps, eye shadow and lipsticks	Orizakwe et al., 2013
UV-VIS spectrophotometry and complexation reactions in solvent mixtures to generate chromophore species	Al, Fe, Cu	Eye shadow	Almeida et al., 2019
Plasma-coupled atomic emission spectrometry (ICP-AES)	Al, Cd, Co, Cr, Cu, Mn, Pb, Ni, Ti	Lipsticks	Liu et al., 2013
Laser Induced Break Spectroscopy (LIBS)	Pb, Cd, Cr, Zn	Batons	Gondal et al., 2010

4 CONCLUSION

The constant and widespread use of cosmetics by the population raises a warning about the potentially toxic and cumulative ingredients that can cause long-term harm. In view of the ability of absorption of toxic metals by the body to reach organs, it brings the concern with the toxicity of these products. In addition, it is necessary to evaluate the safety of the use of these cosmetics as well as the precise knowledge of the concentrations of the ingredients present. In this sense, cosmetic, environmental and social toxicology is of great relevance as it studies the effects of toxicants on cosmetic products as well as on the environment and effects on individuals. Based on the data obtained in the present review, it can be concluded that heavy metals such as lead, aluminum, cadmium are widely present in cosmetics such as lipsticks, eye shadow, eyeliner, creams and may influence the increased risk of diseases such as cancer and other hormonal, behavioral and fertility disorders. Therefore, it is of paramount importance that there is supervision by health agencies in order to ensure safe parameters of cosmetic constituents, for example, through reliable toxicological analytical methods.

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