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Elemental impurities in lipsticks: Results from a survey of the Portuguese and Brazilian markets

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ABSTRACT

For safety reasons, European regulations prohibit the use of a long list of metal(loid)s as ingredients of cosmetic products. However, their presence as impurities in finished products is virtually unavoidable, even under GMP conditions. This study aimed at determining the elemental profile of lipsticks available in the Portuguese and Brazilian markets. A total of 96 lipsticks were purchased in Brazil (n = 53; 9 brands) and Portugal (n = 43; 7 brands) and the content of 44 elements was determined. Results ranged from < 1 µg/g to several tens of µg/g (e.g., Sn, Mn, Zn). Significant differences were found between Portuguese and Brazilian products for several elements, particularly for Pb. For the elements of major toxicological concern (Pb, Cd, As, Sb, Hg), mean values were always below the current limits set by the German competent authority. However, a significant percentage of exceedances were observed for Pb (24%) and Cd (21%). A safety assessment was carried out for the toxicologically relevant elements. Results showed that, except for Pb, the systemic exposure resulting from lipstick use represents less than 0.2% (ca. 3% for Pb) of the respective permitted daily exposure even in the worst-case scenario (i.e., ingestion of the total amount of product applied).

1. Introduction

Cosmetics are highly regulated products in most developed countries. Lipsticks, in particular, because of the potential for systemic exposure through oral ingestion beyond the exposure due to dermal contact, are subject to special attention (European Regulation, 2009; Food and Drugs Act, 2017; U.S Government Publishing Office, 1974).

Regarding elemental species, several metallic elements (e.g., Fe, Zn, Ti, Bi, Cu, Mn) may be present in important amounts in cosmetic products, including lipsticks, since they enter in the composition of ingredients commonly used in the manufacturing of these products. Many others metals and metalloids, on the contrary, due to their well-known toxicity, are strictly prohibited by international regulations. According to the European Regulation No. 1223/2009, a long list of substances (listed in the Annex II) are prohibited in cosmetic products, which includes, in the case of lipsticks, all the compounds of Sb, As, Be, Cd, Cr, Pb, Au, Nd, Te, Tl, Hg and Se (European Regulation, 2009).

However, due to their ubiquitous and persistent nature, the presence of trace amounts of those elements in cosmetic products is virtually unavoidable even under conditions of good manufacturing practices (GMP). In accordance with article 17 of the European Regulation No. 1223/2009, the non-intended presence of small quantities of the prohibited substances (stemming from impurities of natural or synthetic ingredients, the manufacturing process, migration from packaging, etc.) must be limited to the amounts that are technically unavoidable under GMP and, according to article 3 of the same Regulation, cannot compromise the product safety for human health under normal or reasonably foreseeable conditions of use. The safety of each individual cosmetic product has to be demonstrated in the Safety Report, a mandatory component of the respective Product Information File (European Regulation, 2009).

Lead is the element that gave rise to these concerns and has received most of the attention. In 2007, the Campaign for Safe Cosmetics, a coalition of different US entities that works to eliminate substances linked to adverse health impacts from the cosmetics, raised a warning flag when Pb at levels up to 0.65 ppm were found in 61% of the 33 most popular lipstick brands available in the US market (Campaign for Safe Cosmetics, 2007). In 2009, Al-Saleh et al. evaluated the Pb content in lipsticks (n = 26) available in Saudi Arabia market but imported from countries with a low level of regulatory oversight, and identified several

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products containing very high amounts of Pb (three brands with several thousand of ppm). Also in 2009, FDA chemists published the development and validation of a method for the determination of total Pb levels in lipsticks, combining microwave-assisted acid digestion and inductively coupled plasma–mass spectrometry (ICP–MS), and the results of a small survey (20 samples from the USA market) were reported. The average Pb content found was 1.07 μg/g (range: 0.09–3.06 μg/g) (Hepp et al., 2009). Latter, in 2012, the FDA released the results of an expanded survey of the US market, where the levels of Pb were determined in 400 lipsticks, including a variety of shades, manufacturers and price ranges (Hepp et al., 2012). The average Pb content was 1.11 μg/g (range: 0.03–7.19 μg/g), very close to the results found in the initial study. In 2013, a European survey on the content of Pb in 223 lip products (lipsticks and lip glosses from 55 brands; purchased in 15 different European Union countries) was performed, and a mean Pb content of 0.75 μg/g was found (Piccinini et al., 2013). More recently, Brazilian researchers also gave attention to this question and evaluated the Pb content in 21 lipstick samples, reporting values ranging from 0.27 to 4.54 μg/g (Soares and Nascentes, 2013).

However, as mentioned above, in addition to Pb, there is a long list of other elements whose intentional use as ingredients of cosmetic products is prohibited and must be kept at residual levels in the finished products in order to ensure their safety for the consumers.

For the elements of higher toxicological concern (Pb, As, Cd, Hg and Sb) German and Canadian competent authorities conducted specific studies to determine the levels that could be technically achievable is cosmetic products. Based on these studies, the following limits were set: a) Germany (1985) – Pb: 20 μg/g; As: 5 μg/g; Cd: 5 μg/g; Hg: 1 μg/g; Sb: 10 μg/g (BGA, 1985); b) Canada (2012) – Pb: 10 μg/g; As: 3 μg/g; Cd: 3 μg/g; Hg: 1 μg/g; Sb: 5 μg/g (Health Canada, 2012). Last March 2017, German Consumer Protection and Food Safety authority (BVL) have published an up-to-date overview of the technically preventable contents of heavy metals in cosmetic products, and the previous limits were significantly reduced. The new limits were set at Pb: 2 μg/g; As: 0.5 μg/g; Cd: 0.1 μg/g; Hg: 0.1 μg/g; and Sb: 0.5 μg/g, which are 10–50 times lower than the previous ones. These limits were based on the 90th percentile of the dataset obtained in the German Monitoring Scheme (BVL, 2017).

This paper presents the results of two studies on the elemental impurities of lipsticks. The first one corresponds to a study performed on products manufactured in Brazil and commercially available in that country (study BR). The second study was performed in lipsticks available in the Portuguese market, but not necessarily manufactured in Portugal (study PT). The initial idea was also to limit the study to products manufactured in Portugal, but since only two manufacturers were identified, it was decided to include also low cost products (not included in the 2013 European survey), commercially available in “Chinese stores” and low-cost youth fashion and beauty stores. Besides Pb, a wide panel of other elements (43) was determined, including those prohibited by the European Regulation. A comparison was made with the limits set by the German and Canadian authorities. Additionally, a safety assessment was performed to evaluate the potential systemic exposure that may result from the lipsticks use in the worst-case scenario, i.e., assuming the total ingestion of the amount of product applied.

2. Materials and methods

2.1. Samples

The main idea of this study was to determine the elemental impurities in lipsticks actually manufactured in Brazil and Portugal (and not just sold in these markets). Thus, two studies were carried out: (1) Brazilian study – A total of 53 lipsticks were purchased in May/June 2013 at local stores (city of Vitória, Espírito Santo), representing nine brands (from nine different Brazilian manufacturers); (2) Portuguese study – a total of 43 lipsticks were purchased in March/April 2014 at local stores (city of Porto). Since only two Portuguese manufacturers were identified (n = 10 and n = 5 products), it was decided to extend the study to the lower cost products available in the market, independently of the country of origin. These samples include five brands from Chinese manufacture (n = 22 products) and one brand from Turkish manufacture (n = 6 products). These products were obtained at “Chinese stores” and low cost youth fashion and beauty stores. Lipsticks were grouped according to their color in: (1) light pink, (2) dark pink, (3) light brown, (4) dark brown, (5) red and (6) berry. General information about lipsticks in provided in supplementary material (Table S1).

2.2. Sample pretreatment

Lipstick samples were mineralized by closed-vessel microwave-assisted acid digestion in a MLS-1200 Mega (Milestone, Sorisole, Italy) microwave oven equipped with an HPR-1000/10 S rotor and pressure and temperature probes, following the two-step digestion procedure developed and validated by Hepp et al. (2009). Approximately 300 mg of sample was directly weighed into the microwave oven PTFE vessels and 7 mL of concentrated (≥69% w/w) HNO_3 (Trace*SELECT*®; Fluka, France) and 2 mL of concentrated (47–51% w/w) HF (Trace*SELECT*®, Fluka, Germany) were added. Then the vessels were sealed, heated to 130 °C over 15 min and held at this temperature for 3 min. After that, the temperature was ramped to 200 °C over 15 min and held at this temperature for 30 min. After cooling below 50 °C, 30 mL of 4% (w/v) H_3BO_3 (99.999% trace metal basis, Aldrich, St. Louis, MO) were added and the vessels were heated again to 170 °C over 15 min and held for 10 min, to neutralize the remaining HF. Finally, after cooling, the sample solutions were transferred into 50 mL polypropylene volumetric flasks and the volume was adjusted with ultrapure water (resistivity > 18.2 MΩ cm at 25 °C) produced by a Sartorius (Goettingen, Germany) Arium® pro water purification system. One sample blank was included in each microwave-assisted acid digestion run (10 samples).

2.3. Sample analysis

Sample analysis was performed by ICP-MS using an iCAP™ Q (Thermo Fisher Scientific, Bremen, Germany) instrument equipped with a concentric glass nebulizer, a baffled cyclonic spray chamber (Peltier-cooled), a standard quartz torch and a two-cone design (skimmer and sample nickel cones). High-purity (99.9997%) argon (Gasin II, Leça da Palmeira, Portugal) was used as the nebulizer and plasma gas. The equipment control and data acquisition were made through the Qtegra software (Thermo Fisher Scientific, Bremen, Germany). The ICP-MS analysis was carried out under the following conditions: RF power, 1550 W; argon flow rate, 14 L/min; auxiliary argon flow rate, 0.8 L/min; nebulizer flow rate, 1.02 L/min. The following elemental isotopes (*m/z* ratios) were monitored for analytical determination: ^{7}Li, ^{9}Be, ^{51}V, ^{52}Cr, ^{55}Mn, ^{59}Co, ^{60}Ni, ^{65}Cu, ^{66}Zn, ^{73}Ge, ^{75}As, ^{82}Se, ^{85}Rb, ^{88}Sr, ^{90}Zr, ^{93}Nb, ^{98}Mo, ^{107}Ag, ^{111}Cd, ^{118}Sn, ^{121}Sb, ^{125}Te, ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{153}Eu, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{171}Yb, ^{175}Lu, ^{178}Hf, ^{181}Ta, ^{182}W, ^{185}Re, ^{202}Hg, ^{205}Tl, ^{208}Pb and ^{238}U. Indium (^{115}In) was monitored as internal standard.

The instrument was tuned daily for maximum signal sensitivity and stability and low oxide and doubly charged ions formation using a Tune B iCAP Q solution (1 μg/L of Ba, Bi, Ce, Co, In, Li and U in 2% HNO_3 and 0.5% HCl). Calibration standards were prepared by serial dilution of four commercial multi-element standard solutions: *Plasma*CAL SCP-33-MS from SCP Science (Baie-d'Urfé, Quebec, Canada); “Transition metal mix 2”, “metalloid and non-metal mix” and “periodic table mix 3” all TraceCERT® from Fluka, Germany. An internal standard solution was prepared by dilution of a 1000 mg/L indium standard solution (TraceCERT®, Sigma-Aldrich, New Haven, CT), which was then added