Current Topics in
Toxicology
Vol. 18, 2022

Original Article

Analysis of lead and cadmium in cosmetics in Morocco employing differential pulse polarography

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ABSTRACT

Heavy metals are identified as potential impurities and known by their toxicity. This study aims to evaluate the concentrations of lead (Pb) and cadmium (Cd) in facial cosmetic products marketed in Morocco. The lead and cadmium concentrations were analyzed after mineralization with nitric acid, and the content was determined using differential pulse polarography. The analytical method was validated. Linear calibration curves were obtained for Cd (r^2 = 0.998), and for Pb (r^2 = 0.999). For lipsticks just one sample contained lead at 6020 ppm, for foundations one sample contained Pb at 140 ppm, and another sample contained Cd at 50 ppm, for sunblocks just one sample contained Pb at 2350 ppm, and for eye pencils 12 samples contained lead at different concentrations, the median of those being 505 ppm, and just one sample of eye pencil contained Cd at 50 ppm. Comparing our results with the limits recommended in Moroccan regulations, some products are found exceeding these limits. This study showed the presence of heavy metals in some cosmetics. Thus it seems necessary to establish more control in heavy metal levels in cosmetics available on the Moroccan market.

KEYWORDS: cosmetics, lead, cadmium, polarography, heavy metals.

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INTRODUCTION

Cosmetic products include lipsticks, kajal, care creams, face powders, sindoor, eye makeup, talcum powders etc. [1]. The direct application of cosmetics to human skin exposes the latter to the effects of their components. Despite the protective barrier formed by the skin, regular use of these products can expose consumers to both systemic and localized effects like those on the face, the oral cavity, lips, eyes, and mucosa [2-4]. Chronic local exposure and systemic penetration are unavoidable [5]. It should be noted that some products are more critical than others because their oral ingestion or skin absorption is higher due to their application on the lips and the eye area (e.g., lipstick, eye shadow, eyeliners, and mascara). As a result, there is a need to consider the toxic and potentially toxic elements that these types of products may contain [6-8]. Furthermore, metals (mercury, lead, arsenic, and cadmium) can negatively affect critical neurological functions because they cross the blood-brain barrier [9, 10]. Accordingly, awareness of the content of these products in ingredients with intrinsic risk and their exposure levels is necessary. It must be subject to an analysis of the safety of cosmetics [2]. In Morocco, as everywhere in the world, cosmetics are widely used. We conducted this study to assess whether the content of heavy metals in the products complies with the regulations in force. Our study is the first study in Morocco that deals with the analysis of heavy metals in cosmetics (used on the face).

MATERIALS AND METHODS

Choice of Cd and Pb

Lead is one of the most prevalent toxic metals humans are exposed to [11]. Lead and cadmium have no physiological function, and even in small amounts, they are harmful to the body [12, 13]. We reasoned that their levels would provide an initial indication of the purity of cosmetics marketed in our country in terms of heavy metals. On the same reasoning, not being able to analyze all the existing products on the market, we chose the products most commonly used in cosmetics, particularly by women.

Collection of cosmetic samples

Forty-five cosmetic products were chosen from Moroccan markets, including foundations, sunblocks, lipsticks, eye pencils, of different brands, colors, and origins.

Sample preparation using acid digestion procedure

0.5 g of the samples were digested with 5 mL of HNO_3, placed in Pyrex tubes, evaporated in a sand bath until a clear solution was obtained [14], and diluted with HNO_3 up to 5 mL.

Reagents

Lead nitrate, cadmium chloride, nitric acid (65%, supra pure), and potassium chloride were of analytical grade (Merck, KGaA, Darmstadt, Germany).

Instrumentation

For mineralization we used a sand bath which allows heating and homogeneous evaporation of samples. For the analysis of Pb and Cd, we used differential pulse polarography (DPP) which is a susceptible electrochemical method for determining heavy metals in aqueous media [15]. The analyses were performed using 797 VA Computrace (Metrohm, Germany) for polarographic trace; the cell was equipped with three electrodes: the working electrode was a dropping mercury electrode (DME), platinum was used as counter electrode and Ag/AgCl/ (3 M KCl) as reference electrode. Nitrogen was used as an inert gas to operate the mercury electrode and to purge the analyte solutions. The potential was scanned from -0.2 V to -0.7 V with the auto-scan facility. The pulse amplitude was fixed at 50 mV. The electrode drop time was 0.4 s.

Sample analysis

For the electro-analytical determination of lead and cadmium, the polarogram of the individual metal ions in standard solution was obtained using a standard addition procedure as shown in Figure 1 and Figure 2. For sample analysis, 0.5 mL of potassium chloride (KCl) (3 mol/L) as an electrolyte solution was added to 20 mL of distilled water in the polarographic cell. Then 100 µL of the sample was added to this solution and the same analysis procedure was used for the assay of Pb and Cd. Pure nitrogen gas (N_2 at 99.999%) was bubbled for 350 s at a flow rate of 100 ml/min; the nitrogen gas was used to deaerate the cell contents. After the first measurement, the standard addition technique was used for the determination of heavy metals by two-time addition of 100 µL of the standard solution. Then the polarographic cell was exposed to N_2 gas for 20 s to perform the second measurement. After each measurement, the cell and electrode were rinsed. The polarogram gives the concentrations of lead and cadmium in the products, and the polarographic peaks of the analyzed metals in real samples of tested cosmetics were obtained. The standard addition analysis technique was used due to the unavailability of an analyte-free matrix. Each analysis was repeated three times, and "mean ± SD" was obtained by the polarographic peaks.

Method validation

The analysis method was validated, and the lead and cadmium calibration curves were prepared using the standard addition method. To have a concentration range between 50 and 600 ppm for cadmium, and between 10 and 50 ppm for Pb, a known quantity of lead and cadmium standard solutions was added. The precision of the method was expressed as repeatability. The determination of limit of detection (LOD) and limit of quantification (LOQ) was made such that LOD = 3 (σ/S) and LOQ = 10 (σ/S), where σ is the standard deviation and S is the slope of the linear dynamic range.

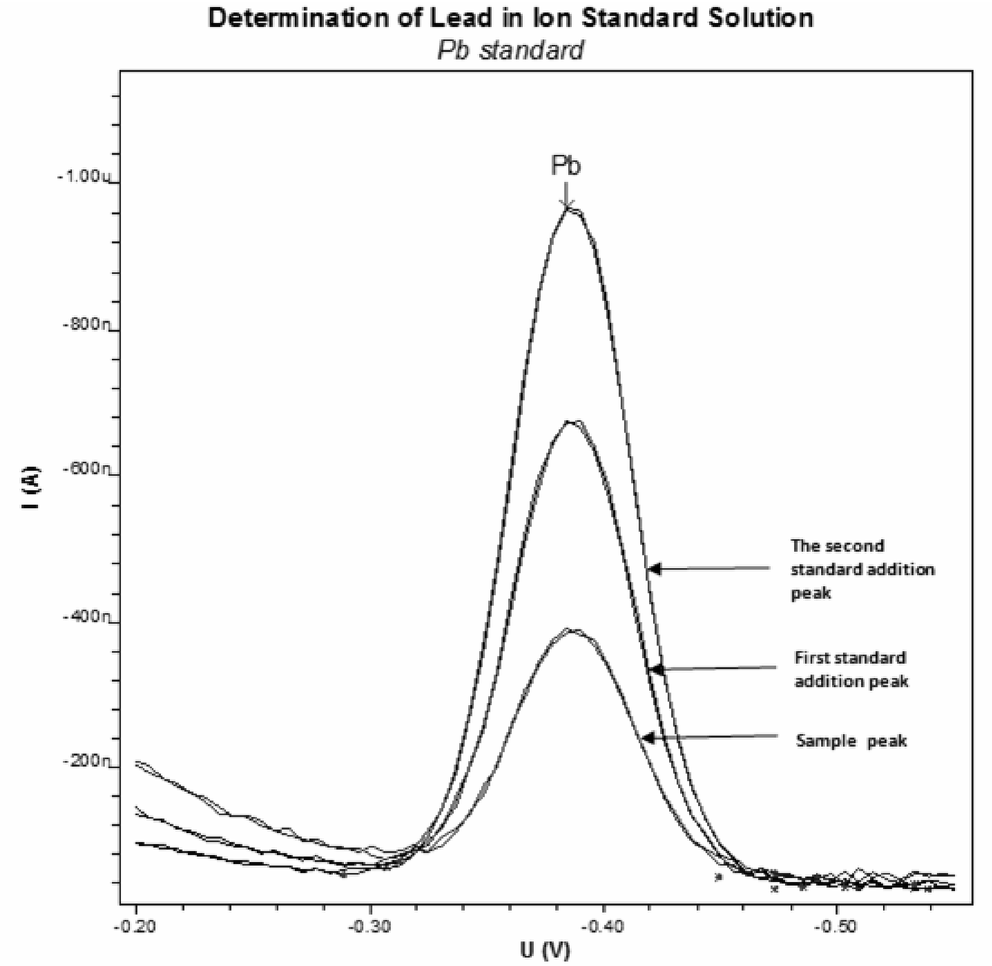

Figure 1. Polarographic peak of differential pulse polarogram (DPP) of lead standard solution.

RESULTS

Method validation

Adequate linear calibration curves were obtained, with correlation coefficient values $r^2 = 0.998$ for Cd and $r^2 = 0.999$ for Pb. LOQ concentration was 0.34 ppm for Pb and 1.67 ppm for Cd. Table 1 presents the results of the analytical validation.

Sample analysis

The products analyzed were divided into 27 eye pencils, 3 sunblocks, 6 foundations, and 9 lipsticks. Among the 9 lipstick samples analyzed, one lipstick sample contained lead. Of the 6 foundation samples analyzed, one sample contained only lead and another sample contained only cadmium. Concerning sunblocks, among the 3 samples analyzed, one sample contained lead and cadmium was not detected on any sample. Regarding the 27 eye pencil samples analyzed, 12 samples contained lead and one contained cadmium. The results obtained are shown in Table 2.

DISCUSSION

In the present study, a high level of lead was detected in some of the tested cosmetics. Concerning lead, the highest concentration (6020 ppm) was detected in a lipstick sample, and the lowest concentration (140 ppm) was detected in a foundation sample. For cadmium, the highest concentration (50 ppm) was in a foundation sample and an eye pencil sample. For the lipstick samples, foundations samples, and sunblocks samples, only one sample of each category

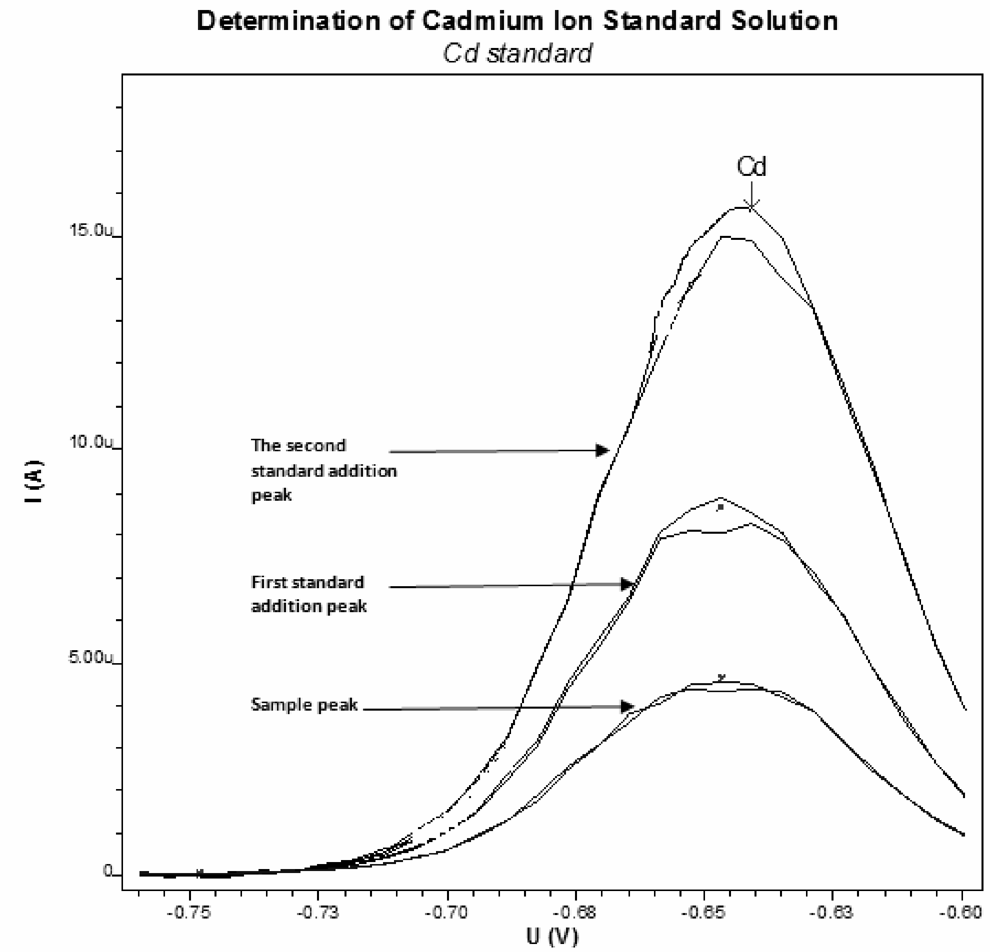

Figure 2. Polarographic peak of differential pulse polarogram (DPP) of cadmium standard solution.

Table 1. Results of the analytical method validation.

Analyte	LOD (ppm)	LOQ (ppm)	Linearity (r^2)	Precision (CV %)	Accuracy (recovery ± RSD)
Pb	0.09	0.34	0.999	0.80	99.98 ± 1.5%
Cd	0.1	1.67	0.998	0.95	100.51 ± 2%

contained lead, with concentrations 6020 ppm, 140 ppm, and 2350 ppm, respectively. However, in the case of the analyzed eye-pencils, 12 samples contained lead, with a median 505 ppm, and a range from 180 ppm to 2280 ppm. Concerning cadmium its concentration (50 ppm) is lower than that of Pb in all the samples analyzed, also we notice that Cd was only detected in one sample of foundations and only one sample of eye-pencils. This result is in accordance with the result of a study in Saudi Arabia which found a higher lead concentration in lipsticks from different markets [16]. The same outcome was reported in Nigeria, in a study conducted on eye pencils and lipsticks [17]. Similarly, in a study conducted in Bulgaria,

Table 2. Concentration of heavy metals in the cosmetic products analyzed.

Type of cosmetics	Number of samples analyzed	Pb		Cd	
		Number of samples containing Lead	Concentration (ppm)	Number of samples containing Cadmium	Concentration (ppm)
Lip sticks	9	1	6020 ± 0.001	0	< LOD
Foundations	6	1	140 ± 0.001	1	50 ± 0.001
Sun blocks	3	1	2350 ± 0.001	0	< LOD
Eye pencils	27	12	505** ± 0.001 (range : [ND-2280 ± 0.001])	1	50 ± 0.001

ND = not detectable = < LOD, **: median.

Pb was considerably higher in lipsticks when compared to other cosmetics analyzed [18]. In Libya, a high concentration of Cd in lipsticks has been reported [19]. The regulation concerning heavy metal content in cosmetics in Morocco is represented by Circular No. 79DMP-00 of December 29, 2016 [20]; this regulation is inspired by the EU model like several countries [21-23]. It provides the regulatory framework and prohibits the use of heavy metals (Cd, Pb, etc.) in cosmetic products [24, 25]. We note that the concentrations of Pb and Cd in some samples exceed the limits recommended by Moroccan regulations. These high concentrations in our samples may be due to the natural presence of certain heavy metals in the raw materials. As reported by Draelos ZD, Cd, Co, Ni, and Pb can be released from the metal equipment used during manufacture and are then found as impurities in the raw materials, mainly in the pigments used in the eye pencils [26, 27]. Rocks, water, and soil can contain heavy metals, and hence traces of heavy metals can be found in the raw materials used to manufacture lipsticks [28].

Finally, the limitation of our study is the number of samples, which does not include all the products available in the Moroccan market. Indeed, this study gives an idea of the concentrations of Pb and Cd in cosmetics marketed in the Moroccan market.

CONCLUSION

This study showed that some cosmetic products marketed in Morocco contain heavy metals. The concentrations of Pb and Cd in some samples of cosmetics exceeded the recommended limits. To protect consumers, laboratory workers can use DPP as an inexpensive technique to more strictly regulate cosmetics. It would seem that this study gives an indication of the safety of cosmetics marketed in Morocco. Further studies are needed to assess the safety of all cosmetic products marketed in Morocco.

CONFLICT OF INTEREST STATEMENT

All authors declare no conflicts of interest.

ABBREVIATIONS

Pb : Lead
Cd : Cadmium
DPP : Differential Pulse Polarography
LOD : Limit of determination
LOQ : Limit of quantification
SD : Standard Deviation

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