Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) for Tracing the Levels of Heavy Metals in Lipstick

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Abstract

Analysis of lipstick for heavy metals (lead, cadmium and mercury) by inductively coupled plasma optical emission spectrometry (ICP-OES) was carried out. A total of 30 lipsticks from different brand categories sold in the local markets in Khon Kaen province of Thailand were included in this study. The lipstick samples were extracted with a chloroform/methanol/nitric acid/water solution (50:20:15:15, v/v/v/v) at ambient temperature for 48 h and subjected to ICP-OES analysis. The lipstick samples were free of mercury while lead and cadmium were detected. Lead content was detected in all lipstick samples with a concentration range of 1.991-19.186 mg/kg whereas only one lipstick sample was found to contain cadmium (0.035 mg/kg). Even though the level of lead detected in lipsticks in this study was within the safe permissible limit of Thailand and USA, due to its cumulative toxic effects prolonged exposure to lead may cause adverse health problems in pregnant and breastfeeding women since lead could be allocated through placenta and milk.

Keywords: Heavy metals, ICP-OES, Lipstick

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การใช้เทคนิค Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) หาปริมาณโลหะหนักในลิปสติก

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บทคัดย่อ

การศึกษานี้มีวัตถุประสงค์เพื่อวิเคราะห์ปริมาณโลหะหนัก (ตะกั่ว แคดเมียม และปรอท) ในตัวอย่างลิปสติกด้วยวิธี inductively coupled plasma optical emission spectrometry (ICP-OES) โดยใช้ตัวอย่างลิปสติกทั้งหมด 30 แท่ง จากทั้งหมด 5 ยี่ห้อที่ขายตามท้องตลาดในจังหวัดขอนแก่น ประเทศไทย ทำการสกัดตัวอย่างลิปสติกที่อุณหภูมิห้องเป็นเวลา 48 ชั่วโมงในตัวทำละลายคลอโรฟอร์ม/เมทานอล/กรดไนตริก/น้ำ (50:20:15:15) และทำการวิเคราะห์ปริมาณโลหะหนักด้วยวิธี ICP-OES พบว่าลิปสติกไม่มีการปนเปื้อนของปรอทแต่มีการปนเปื้อนของตะกั่วและแคดเมียม โดยพบการปนเปื้อนของตะกั่วในลิปสติกทุกแท่งที่ทำการศึกษาในช่วงความเข้มข้น 1.991-19.186 มก./กก. ในขณะที่มีการปนเปื้อนของแคดเมียมในลิปสติกเพียงหนึ่งแท่ง (0.035 มก./กก.) แม้ว่าระดับตะกั่วที่ตรวจพบในลิปสติกในการศึกษานี้มีค่าไม่เกินมาตรฐานของประเทศไทยและสหรัฐอเมริกาการได้รับตะกั่วเป็นเวลานานอาจทำให้เกิดพิษสะสมในร่างกายได้ โดยเฉพาะหญิงมีครรภ์และหญิงให้นมบุตรเนื่องจากตะกั่วสามารถผ่านทางรกและน้ำนมได้

คำสำคัญ: โลหะหนัก ICP-OES ลิปสติก

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Introduction

Lipstick is the basic daily product that is included in face makeup application, in addition to face powder, foundations, eye shadows, and blush[1]. Many metallic-based colors, which may contain lead and other heavy metals, are used as dyes in cosmetic products, including lipstick[2,3]. Lipsticks with metallic-based colors are believed to contain heavy metals such as lead, nickel, aluminum, arsenic, cadmium, antimony, and chromium[4]. Moreover, heavy metals can be released by the metallic devices used during the manufacturing of products[5].

Even though lipstick consumers are exposed to heavy metals in small amounts on a daily basis, repeated applications with a prolonged exposure period of wearing time can result in significant cumulative exposures for the user and individuals that come in contact with the user[6,7]. Potential routes of metal exposure include incidental ingestion from applied lipstick in female adults, subsequent maternal transfer to the fetus, and also small children who accidentally ingest lipstick products[7].

Heavy metals like lead, cadmium, chromium and mercury are very toxic contaminants. Their excessive bioaccumulation can cause profound biochemical changes inside the human body and produce both chronic and acute health consequences including kidney dysfunction, polycythemia, bone fracture, respiratory toxicity, memory deterioration, asthma, heart problems and various kinds of cancers[8-15]. Moreover, mercury may damage the brain and the health of developing fetus[16].

Several studies have attempted to examine the contamination of heavy metals in lipsticks. For example, Chen *et al*. evaluated the concentration of lead in seven lipstick samples using flow injection chemical vapor generation isotope dilution inductively coupled plasma mass spectrometry[17]. Zakaria and Ho also determined the contents of lead, cadmium and chromium in 15 different brands of lipsticks sold in the Malaysian market and found a concentration range of lead, cadmium and chromium of 0.77-15.44, 0.06-0.33 and 0.48-2.50 mg/kg, respectively[6]. Moreover, the levels of lead, cadmium, nickel, chromium, mercury, antimony, and arsenic in 14 brands of lipsticks were assessed in Saudi markets[4]. To our knowledge however, the concentrations of heavy metals in lipstick manufactured and/or sold in Thailand have been rarely reported with only a previous study by Al-Saleh *et al*.[18] revealing a lead concentration range of 0.36-0.65 ppm wet weight in lipsticks from Thailand. Therefore, investigating the levels of heavy metals in lipstick samples sold in local markets of Thailand is of great importance.

In this study, 30 lipstick samples from five different brand and color categories were purchased from the local markets in Khon Kaen province of Thailand and analyzed for heavy metals (lead, cadmium and mercury) by inductively coupled plasma optical emission spectrometry (ICP-OES).

Materials and methods

Chemicals

ICP quality standards of lead, cadmium and mercury were purchased from Merck (Germany). All chemicals used for extraction were of analytical grade, purchased from Merck (Germany).

Study design

The study was carried out at Khon Kaen University, Thailand, and 43 questionnaires were distributed to the female employees in the university to gain the information about lipsticks. The target lipstick samples were purposely purchased in January 2015 based on the popularity among respondents from the female staff that applies lipstick regularly and only the top five lipstick brands were chosen for analysis. Ten lipstick samples of different brands and colors were analyzed in triplicates (each using only one lipstick sample) that made up a total of 30 samples in this study.

Acid digestion

About 0.5 g of each lipstick sample was weighed and extracted at ambient temperature with a chloroform/ methanol/ nitric acid/ water (50:20:15:15, v/v/v/v) solution for 48 h. Following thorough mixing, deionized water was added to the mixture to a final volume of 100 mL. The mixture was then filtered through a No. 1 Whatman filter paper and the filtrate was collected for analysis of heavy metals.

Inductively coupled plasma optical emission spectrometer (ICP-OES)

Optima 2100 DV ICP-OES (Perkin Elmer, USA) was used for all metal-determinations in the lipstick samples. The operation conditions and the wavelengths are summarized in Table 1. The instrument was calibrated using a five-point calibration curve: 0.1, 0.5, 1, 2 and 4 mg/L for lead and mercury; 0.04, 0.2, 0.4, 1 and 2 mg/L for cadmium.

Table 1 Instrumental and operating conditions for ICP-OES measurements.

Parameter	Value
Radio frequency power (kW)	1.2
Plasma viewing	Axial
Coolant gas (Ar) flow rate (L/min)	10.5
Auxiliary gas (Ar) flow rate (L/min)	0.5
Nebulizer flow rate (L/min)	0.38
Read time	min 2 sec, max 5 sec
Wavelength (nm)	Pb 220.353, Cd 228.802, Hg 184.950

Quality control

The limit of detection (LOD) and limit of quantification (LOQ) were calculated with three and ten times the standard deviation of the 10 individually prepared method blank solution. Extraction recovery was evaluated by spiking three replicates of blank matrix with heavy metal standards. The percent of extraction recovery was calculated by comparing the concentration of heavy metals before the acid digestion to its concentration spiked after digestion in the blank matrix using the Equation: Recovery (%) = (B/A) × 100, where, A denotes the concentration of each element after digestion and B represents the concentrations before digestion. The instrument was calibrated with each element at a five-point calibration curve. Linearity of each element was tested from 0.04 to 4 mg/L. Linearity of the calibration curve for each element was evaluated by the coefficient determination (R^2). Identical samples were analyzed three times within one day's acquisition sequence. Each brand of lipstick was analyzed in triplicates in order to gain a more precise estimation of the data.

Statistical analysis

The results are expressed as means ± SD of three replicates and the obtained data were analyzed using one-way analysis of variance (One-way ANOVA) with Duncan's multiple range test (SPSS version 17.0) to determine the differences of the heavy metal concentrations among different lipstick samples at a significance level of $p < 0.05$.

Results and discussion

Quality control

Linear range, linearity, recovery, LOD, and LOQ for all the target elements are shown in Table 2. The average

extraction recovery for lead, cadmium and mercury was 95.9%, 99.9% and 101.6%, respectively. The five-point calibration curve showed good linearity over the concentration range from 0.04 to 4 mg/L where correlation coefficients (R^2) ranged from 0.9995 to 1.0000.

Concentration of heavy metals in lipstick samples

The concentrations of heavy metals in the lipstick samples of different brand and color categories are summarized in Table 3. The lipstick samples were free of mercury but contaminated lead and cadmium. Only one lipstick sample (W2) was contaminated with cadmium with a low concentration of 0.035 mg/kg. The level of cadmium in lipsticks reported in this study was lower than in the study by Zakaria and Ho[6]. Gondal *et al*. also examined the content of cadmium in lipsticks from different cosmetic shops in the Kingdom of Saudi Arabia and reported much higher cadmium contents in the lipstick samples (5.4-10.6 ppm)[19].

Lead contamination in cosmetics especially lipstick has raised concerns over human health risks and was therefore gained much attention from researchers all over the world[3,7,20]. In the current study, lead contamination was detected in all lipstick samples with a concentrations range of 1.991-19.186 mg/kg with the highest lead content observed in the lipstick sample M2 (19.186), followed by W2 (15.619), L2 (13.107) and W1 (13.028), indicating that lead was most abundant in lipsticks with metallic-based colors. Most lipstick samples from different bands showed significant ($p < 0.05$) differences in the level of lead while some exhibited the same lead level. On the other hand, the lead content was significantly ($p < 0.05$) different as observed for the lipsticks from the same brand, which might be due to their differences in metallic-based colors. The content of lead in lipsticks in this study was higher than the concentration reported by Gondal *et al*.[19], in which the level of lead in lipstick was found to range from 6.4 to 9.9 ppm. Another study by Gunduz and Akman also showed lower concentrations of lead (0.11-4.48 mg/kg) in 25 lipstick samples, measured by solid sampling high resolution continuum source electrothermal atomic absorption spectrometry[20]. Besides, lower lead contents in lipsticks were previously reported by Soares and Nascentes (0.27-4.54 mg/kg)[21] and Piccinini *et al*. (0.04-3.75 mg/kg)[1]. However, the content of lead in lipsticks this study was lower than the content reported by Al-Saleh et al.[3]

Table 2 Linear range, linearity, recovery, LOD and QOD for three target elements.

Element	Linear range (mg/L)	R^2	Recovery ±RSD (%) (*n* =7)	LOD (mg/kg)	LOQ (mg/kg)
Pb	0.1-4	1.0000	95.9 ± 5.00	2.04	8.00
Cd	0.04-2	1.0000	99.9 ± 3.52	0.06	3.00
Hg	0.1-4	0.9995	101.6 ± 4.21	0.37	8.00

LOD: limit of detection; LOQ: limit of quantification.

Table 3 Concentrations of lead (Pb), cadmium (Cd) and mercury (Hg) in the lipstick samples (*n* = 3).

Brand category	Color shade	Pb† (mg/kg)	Cd (mg/kg)	Hg (mg/kg)
Brand I				
M1		8.005 ± 1.320[d]	ND	ND
M2		19.186 ± 2.146[a]	ND	ND
Brand II				
R1		1.991 ± 1.179[g]	ND	ND
R2		4.286 ± 0.462[f]	ND	ND
Brand III				
A1		5.922 ± 2.688[e]	ND	ND
A2		3.627 ± 1.651[f]	ND	ND
Brand IV				
L1		8.41 ± 4.198[d]	ND	ND
L2		13.107 ± 0.797[c]	ND	ND
Brand V				
W1		13.028 ± 1.049[c]	ND	ND
W2		15.619 ± 1.194[b]	0.035 ± 0.0087	ND

ND: not detected
Value = Mean ± SD
†Data followed by different letters were statistically different at $p < 0.05$.

Even though the concentrations of lead in lipsticks in the present study were higher than those reported by previous studies, they were not higher than the safe permissible lead limit set by the United States Food and Drug Administration (20 ppm)[6]. However, four lipstick samples (M2, W2, L2 and W1) were observed to contain lead with the concentrations that exceeded the Health Canada permissible limit (10 ppm)[6]. It is important to bear in mind that the level of heavy metals reported in this study was determined based on a low number (30) of lipstick samples;

accordingly, to make the representative data more reliable a greater number of lipstick samples should be considered.

Though the Guidelines of Control of Cosmetic Products has been launched in Thailand, the existence of heavy metals might be due to contamination of the lipstick manufacturing process, in which the heavy metals sources might come from solder, leaded paints on manufacturing equipment, and also from lead-contaminated dust from the manufacturing surroundings. Even though the level of lead reported in this study was within the safe permissible limit, due to its cumulative toxic effect prolonged exposure to lead may cause adverse health problems in pregnant women and breastfeeding women since lead can be allocated through placenta and milk.

Conclusions

The lipstick samples were purchased from the local markets in Khon Kaen province of Thailand, and the concentrations of lead, cadmium and mercury were quantified by ICP-OES. The results revealed that the lipstick samples were free of mercury but contaminated with lead and cadmium. Only one sample was found to contain a low concentration of cadmium. Meanwhile, all the lipstick samples tested were contaminated with lead with high levels of lead contamination observed in four samples. Statistical analyses showed that there was a significant difference of lead content in the lipsticks of different brands. Meanwhile, the lipsticks of the same brand also showed significant differences in lead content, which might be due to their differences in metallic-based colors.

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