Original Article

การวิเคราะห์ปริมาณตะกั่วในเครื่องสำอาง โดยเทคนิคอะตอมมิกแอบซอบชั่นสเปกโทรโฟโทเมตรี

สุทธาพร วงศ์กาพสินธุ์[1*], วิรัช เรืองศรีตระกูล[2]

Received: 25 January 2017 **Accepted:** 23 March 2017

บทคัดย่อ

บทนำ: งานวิจัยนี้ได้ศึกษาปริมาณของโลหะตะกั่ว ซึ่งมีโอกาสจะปนเปื้อนอยู่ในตัวอย่างประเภทเครื่องสำอาง ตัวอย่างที่ทำการศึกษาแบ่งเป็นสี่ประเภท ได้แก่ อายแชโดว์ ผลิตภัณฑ์ย้อมสีผม อายไลเนอร์ และสบู่เพื่อความงาม ตามประกาศกระทรวงสาธารณสุข ประเทศไทย เรื่อง ชื่อวัตถุที่ห้ามใช้เป็นส่วนผสมในการผลิตเครื่องสำอาง พ.ศ. 2559 ได้กำหนดไว้ว่าปริมาณการปนเปื้อนของตะกั่วต้องไม่เกิน 20 ส่วนในล้านส่วนโดยน้ำหนัก โดยการศึกษานี้จะใช้เทคนิคอะตอมมิคแอบซอบชั่นสเปกโทรโฟโทเมตรีในการตรวจวัดปริมาณตะกั่ว **วิธีดำเนินการวิจัย:** ตัวอย่างเครื่องสำอางจะถูกเตรียมโดยใช้เทคนิคการย่อยตัวอย่างด้วยกรดไนตริก สารละลายใสที่ได้จากการย่อยตัวอย่าง จะนำไปวัดค่าการดูดกลืนคลื่นแสงจากอะตอมอิสระของโลหะตะกั่วที่เกิดขึ้น ใช้ความยาวคลื่นที่เหมาะสมในการตรวจวัดปริมาณตะกั่วที่ 283.31 นาโนเมตร กราฟมาตรฐานของสารละลายมาตรฐานตะกั่วถูกสร้างขึ้นในช่วงความเข้มข้น 0.25 – 3.0 ไมโครกรัมต่อมิลลิตร ทุกตัวอย่างจะทำการวิเคราะห์ซ้ำจำนวน 3 ครั้ง **ผลการวิจัย:** จากตัวอย่างเครื่องสำอางที่ทำการศึกษาจำนวน 80 ตัวอย่าง พบว่าค่าเฉลี่ยปริมาณสูงสุดมาจากตัวอย่างประเภทอายแชโดว์ ปริมาณตะกั่วที่ตรวจพบจากตัวอย่างอายแชโดว์ ผลิตภัณฑ์ย้อมสีผม อายไลเนอร์ และสบู่เพื่อความงาม มีค่าความเข้มข้นอยู่ในช่วง 1.58 – 17.53, – 0.001.19, 0.00 – 7.07 และ 0.051 – .17 ไมโครกรัมต่อกรัม ตามลำดับ และพบค่าเฉลี่ยของปริมาณตะกั่วเท่ากับ 4.88, 0.30, 1.07 และ 0.64 ไมโครกรัมต่อกรัม ตามลำดับ **สรุปผลการวิจัย:** ผลการศึกษาแสดงว่าปริมาณตะกั่วที่พบไม่ได้เกินระดับความปลอดภัยที่กำหนดไว้โดย ประกาศกระทรวงสาธารณสุข ประเทศไทย

คำสำคัญ: เครื่องสำอาง, ตะกั่ว, อะตอมมิคแอบซอบชั่นสเปกโทรโฟโทเมตรี

วารสารเภสัชศาสตร์อีสาน 2560; 13 (ฉบับพิเศษ): 34-40

[1] นักศึกษาระดับบัณฑิตศึกษา คณะเภสัชศาสตร์ มหาวิทยาลัยขอนแก่น อ.เมือง จ.ขอนแก่น

[2] Ph.D. รองศาสตราจารย์, อาจารย์ประจำสาขาวิชาเภสัชเคมี คณะเภสัชศาสตร์ มหาวิทยาลัยขอนแก่น อ.เมือง จ.ขอนแก่น

* **ติดต่อผู้นิพนธ์**: สุทธาพร วงศ์กาพสินธุ์ คณะเภสัชศาสตร์ มหาวิทยาลัยขอนแก่น อำเภอเมือง จังหวัดขอนแก่น 40002
โทร. 043-202378, โทรสาร. 043-202379, e-mail: suttaporn10@gmail.com

Determination of lead in cosmetics using atomic absorption spectrophotometry

Suttaporn Wongkalasin[1*], Wirat Ruengsitagoon[2]

Abstract

Introduction: This study investigated the level of lead (Pb), a heavy metal which was possible to contaminate in cosmetic samples. All samples were classified into four groups; eye shadow, hair dye, eye linear and beauty soap. Announcement of The Ministry of Public Health (the component name not to be used as an ingredient in cosmetics), BE2559 (2016), Thailand, indicated that the safety level for lead contamination should not be higher than 20 ppm by weight. The technique for this studied was atomic absorption spectrophotometric method. **Methods:** The cosmetic samples were prepared using digestion technique with nitric acid. The clear solution of digested samples was determined for lead (Pb) level by investigating light absorption of lead free atom. The appropriate wavelength was at 283.31 nm. The calibration curve was linear over the range of 0.25 – 3.0 µg mL^{-1} lead standard solution. These samples were analyzed triplicate. **Results:** From 80 cosmetic sample, it was found that the highest average lead level obtained from eye shadow sample. The lead levels was shown in the range of 1.58 – 17.53, – 0.001.19, 0.00 – 7.07 and 0.05 – 1.17 µg g^{-1} for eye shadow, hair dye, eye linear and beauty soap, respectively. The average lead level were found to be 4.88, 0.30, 1.07 and 0.64 µg g^{-1} for eye shadow, hair dye, eye linear and beauty soap, respectively. **Conclusion:** All lead levels in this study were not higher than the safety limit of announcement from The Ministry of Public Health, Thailand.

Keywords: Cosmetics, Lead, Atomic absorption spectrophotometry

IJPS 2017; 13 (Supplement): 34-40

[1] Graduate student, Faculty of Pharmaceutical Sciences, Khon Kaen University, Khon Kaen.

[2] Ph.D. Associate Professor, Department of Pharmaceutical Chemistry, Faculty of Pharmaceutical Sciences, Khon Kaen University, Khon Kaen

* **Corresponding author:** Suttaporn Wongkalasin, Faculty of Pharmaceutical Sciences, Khon Kaen University, Khon Kaen 40002, Tel: 043-202378, Fax: 043-202379; e-mail: suttaporn10@gmail.com

Introduction

Under the European Council Directive 76/768/EEC, a cosmetic includes any substance or mixture of substances manufactured, sold or represented for use in cleansing, improving or altering the skin, hair, lips, nails or teeth. This definition includes a myriad of products used by men and women; skin care, lotions, lipsticks, eye and facial makeup, permanent waves, hair dye and beauty soap (European Union, 1976).

Lead contamination of cosmetics may originate from leaded paint in production equipment or from contaminated dust. Cosmetics also may be contaminated with lead if they are manufactured with ingredients that naturally contain lead or are produced under conditions that could introduce lead into the ingredients. Dyes and pigments used as ingredients in cosmetics are regulated as color additives by the FDA and must undergo pre-market approval by the agency before they may be used in any cosmetics. The evidence of lead potential to cause harm is well known (Salvador *et al*., 2007).

This study wants to find out the level of lead (Pb) which were possible to contaminate in cosmetic samples including eye shadows, hair dye, eye linear and beauty soap. Announcement of Thai ministry of public health and the regulation of ASEAN (Association of Southeast Asian Nations) indicated that the safety level of lead contamination should not be higher than 20 ppm by weight (Announcement of Thai ministry of public health, 2016; ASEAN Cosmetic Directive, 2017). Only Canada uses lead (Pb) level 10 μg g^{-1} as its safety threshold (Bocca *et al*., 2014). Several methods have been reported previously for the determination of lead (Pb) heavy metal in cosmetic including flame atomic absorption spectrophotometry (Sani *et al*., 2016), graphite furnace atomic absorption spectrophotometry (Soaes *et al*., 2013), electrochemical method (Panigati *et al*., 2002) and inductively coupled plasm - coupled with mass spectrometry (Volpe *et al*., 2012). Flame atomic absorption spectrophotometric method is a widely method used for heavy metal determination. Its advantages of relatively simple operation and high sensitivity are from the measurement of the amount of energy absorbed by the sample in flame. The optimum wavelength for determination of lead (Pb) was at 283.31 nm. (Sani *et al*., 2016; Khantivong, 2016).

Materials and Methods

Instrumentations

1) Atomic absorption spectrophotometer, PinAAcle 900F, PerkinElmer®; USA.

2) Electrodeless discharge lamp (EDL) for Pb, PerkinElmer®; USA.

3) Sample preparation digestion block, SPB 100-12, PerkinElmer®; USA.

4) Deionized distillated water unit, Millipore Milli-Q; USA.

Chemicals

1) Nitric acid (HNO_3), AR grade, J.T. Baker; USA.

2) Standard solution of lead (Pb), 1000 µg mL^{-1}, for atomic absorption spectrometry, AR grade, BDH; UK.

Sample Collection

Cosmetic samples were collected using simple random technique from open markets and cosmetic shops in Udon Thani province. All samples (80) were classified into four groups which were eye shadow, hair dye, eye linear and beauty soap.

Sample Preparation

Each cosmetic sample was weighted 3 g using top-loading balance and transferred into 100 ml digestion vessels. The solution of nitric acid (50% v/v) 40 mL was added into vessel tube which were heated by digestion block at 110 ^{o}C for 2-3 hrs. These sample solutions were leaved to cool down at room temperature and transferred all of solution into 25 mL graduated volumetric flask. Then, sample solution was adjusted volume to 25 ml with deionized distillated water and transferred the appropriate sample volume to the centrifuge tube. Finally, the clear solution was separated by centrifuge at 4,000 rpm for 3 minutes, and took it to analyze with atomic absorption spectrophotometer (Ozbek et al., 2016; Khantivong, 2016). Figure 1 were shown sample preparation and measured procedure for lead determination. These samples were analyzed triplicate.

(a) (b)

Figure 1 Sample preparation and measured procedure
(a) Digestion of samples using digestion block
(b) Flame atomic absorption spectrophotometer

Preparation of lead standard solution

The 50 µg mL^{-1} lead standard stock solution was prepared by pipette 5 mL of lead standard solution 1000 µg mL^{-1} into 100 mL graduated volumetric flask. The solution was then adjusted volume to 100 mL with deionized distillated water. The working standard solution was prepared by diluting the 50 µg mL^{-1} lead standard solution to appropriate concentration of 0.25, 0.50, 0.75, 1.0, 2.0 and 3.0 µg mL^{-1}. The working standard solution was freshly prepared each day to constructed the calibration curve including calculated correlation coefficient (r^2) and linear regression equation of the standard calibration curve. The appropriate wavelength for lead (Pb) heavy metal determination was 283.31 nm using flame atomic absorption spectrophotometer.

Results

Table 1 Lead level in cosmetic samples

Sample Code	Eye Shadow	Hair Dye	Eye Linear	Beauty Soap
	Lead level founded (μg g^{-1})			
01	2.95	0.25	ND	0.60
02	5.01	0.34	ND	0.74
03	3.23	ND	0.17	0.77
04	3.50	1.19	ND	0.76
05	3.45	0.30	0.38	0.81
06	8.07	0.46	1.71	0.93
07	5.52	0.38	5.00	1.03
08	6.27	0.48	6.58	1.17
09	4.65	0.60	0.48	0.82
10	3.13	0.68	7.07	1.10
11	1.58	ND	ND	0.56
12	5.59	0.27	ND	ND
13	17.53	0.27	ND	0.50
14	3.21	0.20	ND	0.44
15	6.55	0.18	ND	0.77
16	3.71	ND	ND	0.36
17	1.82	0.22	ND	0.36
18	4.70	ND	ND	0.33
19	2.92	0.24	ND	0.31
20	4.17	ND	ND	0.53

ND : Not detected

Using the proposed method for determination of lead level under the optimum conditions, the linear calibration graph over the appropriate range was established and the regression equation could be expressed as $y = 0.0195x - 0.0004$ (r^2: 0.9993, n=7). Percentage recoveries of 1.0 and 3.0 μg mL^{-1} of lead solution were found to be 102.16 ± 2.50 % and 99.68 ± 1.53 % (n=7), respectively. The limits of detection (LOD=3(σ/s)) and the limit of quantification (LOQ=10(σ/s)) for the lead determination were 0.05 and 0.17 μg mL^{-1}, respectively. Where σ is the standard deviation of the blank (n=5) and s is the slope of the calibration curve.

Table 2 Analytical characteristics of lead level

Samples (*n*=20)	Lead level founded (μg g^{-1}) Eye Shadow	Hair Dye	Eye Linear	Beauty Soap
Contaminated sample (*n*)	20	15	7	19
Pb in range of (μg g^{-1})	1.58 –17.53	0.00 –1.19	0.00 – 7.07	0.05 – 1.17
Average of Pb level (μg g^{-1})	4.88 ± 3.39	0.30 ± 0.29	1.07 ± 2.28	0.64 ± 0.30

The lead levels from 80 cosmetic samples were lower than the safety level established by The Ministry of Public Health of Thailand (20 ppm by weight). Interestingly, 61(76.25%) cosmetic samples were contaminated with lead heavy metal (Table 1).

The lead concentration were found in the range of 1.58 – 17.53, – 0.001.19, 0.00 – 7.07 and 0.05 – 1.17 μg g^{-1} for eye shadow, hair dye, eye linear and beauty soap, respectively. The average of lead level were shown to be 4.88, 0.30, 1.07 and 0.64 μg g^{-1} for eye shadow, hair dye, eye linear and beauty soap, respectively (Table 2).

Discussions and Conclusion

The 80 samples of cosmetic sample was found the highest average of lead level which came from eye shadow samples. On the other hand, It was found that the lowest average of lead level was gave when analysis hair dye samples. These studied had shown the level of lead not higher than the safety limit by announcement of The Ministry of Public Health, the component name not to be used as an ingredient in cosmetics, BE2559(2016), Thailand.

Acknowledgments

The authors are grateful to the Pharmaceutical Chemistry Department, Faculty of Pharmaceutical Sciences of Khon Kaen University for partials support.

References

Announcement of the Food and Drug Administration's Statement of the Ministry of Public Health (the component name not to be used as an ingredient in cosmetics), Thailand, BE2559 (2016); page 13.

ASEAN Cosmetic Directive [online]. [Cited 2017 Mar 13]. Available from: http://has.gov.sg/content/hsa/en/Health_Products_Regulation/Cosmetic_Products/Overview/ASEN_Cosmetic_Directive.html

Bocca B, Pino A, Alimonti A, Forte G. Toxic metals contained in cosmetics. *Regul Toxicol Pharm.* 2014; 68: 447-467.

EU, European Union. Council Directive 76/768/EEC on the approximation of the laws of the member states relating to cosmetic products. *Official Journal L*. 1976; 262:p.169 .

Khantivong, C. Heavy metals level contamination in traditional medicine from Lao PDR. A thesis for the degree of Master of Science in Pharmaceutical Chemistry and Natural Products, Khon Kaen University, 2016.

Ozbek N, Akman S. Determination of lead, cadmium and nickel in hennas and other hair dyes sold in Turkey. *Regul Toxicol Pharm*. 2016; 79: 46-53.

Panigati M, Piccone M, D'Alfonso G, Orioli M, Carini M. Determination of lead and cadmium in titanium dioxide by differential pulse anodic stripping voltammetry. *Talanta*. 2002; 58: 481-488.

Salvador A, Chisvert A. Analysis of cosmetic products. Amsterdam, Elsevier, 2007.

Sani A, Gaya MB, Abubakar FA. Determination of some heavy metals in selected cosmetic products sold in Kano metropolis, Nigeria. *Toxicol Rep*. 2016; 3: 866-869.

Soares AR, Nascentes CC. Development of a simple method for the determination of lead in lipstick using alkaline solubilization and graphite furnace atomic absorption spectrometry. *Talanta*. 2013; 105: 272-277.

Volpe MG, Nazzaro M, Coppola R, rapuano F, Aquino RP. Determination and assessments of selected heavy metals in eye shadow cosmetics from China, Italy and USA. *Microchem J*. 2012; 101: 65-69.