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Analysis of Lead (Pb) and Cadmium (Cd) in Whitening Creams using Atomic Absorption Spectroscopy

A. T. Agustina*, M. P. Primadi, H. Randhanugraha, K. Khotimah, and I. Luriyani

Department of Chemistry Education, Universitas Negeri Yogyakarta

Article Info	ABSTRACT	
Article history:	This research aims to determine the concentration of Lead (Pb) and Cadmium (Cd) metals contained in face whitening creams that are	
Received: Oct 12th, 2019	sold in store around Sleman, Yogyakarta. The analysis concentration	
Revised: Nov 20th, 2019	of Pb and Cd levels in those whitening creams carried out using	
Accepted: Nov 26 th , 2019	Atomic Absorption Spectrophotometer (AAS) at Chemistry laboratory of Faculty of Mathematics and Natural Sciences, Universitas Negeri Yogyakarta. We used 5 different face whitening cream samples (here after indicated by sample A, B, C, D, E) that taken randomly with the range price of thousand rupiahs. The results of	
*Corresponding Author:	analysis showed that in the sample A contains of -0.729 ppm Pb and	
Anisa Tri Agustina, Dept. of Chemistry Education Universitas Negeri Yogyakarta	1,199 ppm Cd; sample B covers 0,017 ppm Pb and 1,274 ppm Cd; in the sample C consists of 1,082 ppm Pb and 1,254 ppm Cd; in the sample D contains a total of 1.242 ppm Pb and 1.215 ppm Cd; and in the sample E consists of -0.409 Pb and 1.232 ppm Cd. The results of	
Email: anisatasata@gmail.com	this research are useful as the bases of their heavy metal concentrations, thus the possibilities of counterfeiting of the products ingredients can be avoided. An effort should be made in order to tell the customers about the harmful effects of over consumption of the face whitening cream with heavy metal acumulations in the body.	
	Keyword: whitening creams, lead metal, cadmium metal	

1. INTRODUCTION

Cosmetics are closely related to beauty, because through cosmetics a person can express his beauty (Sankaranarayanan, 2017). Cosmetics are generally used for the human body with the aim of cleaning, beautifying, attracting appearance, and whitening the skin (Mansor, Mat Ali, & Yaacob, 2010). The cosmetics are also used to protect the skin from UV rays, attract an attention, follow the evolving fashion, and look more beautiful (Tejal et.al, 2013). Further, the cosmetic is an ingredient used for the entire human body especially outside of the body. The use of cosmetics could enhance one's beauty, appearance, and self-confidence (Raja et.al, 2016). However, the cosmetics were made by various chemicals and some of them may contain harmful chemicals (Khad & Nature, 2019).

Several products of cosmetic e.g., perfume, nail polish, lotion etc. can cause harmful effects (Dooms-Goosens, 1993) such as irritations, allergies (Nigam, 2009), photosensititation, acne (Puraningdyah & Nelva, 2013), intosication and bacterial infections (Al-Hoqail, 2003). Therefore, as an effort to bring the cosmetics is safely to be used, the Indonesian government have made provisions and minimum standard of the metal contained in the cosmetics. That is the regulation of National Agency of Drug and Food Control (BPOM RI) Number 17 of 2014 regarding the requirements for contamination of microbes and heavy metals in cosmetics, the limitation of Pb and Cd in a cosmetic should be < 20

mg/kg and < 5 mg/kg repectively. Even other countries such as Germany have the same limits on Pb and Cd metal in a cosmetic and this is carried out by the German state (Bautista, Serrano-Fragoso, & Miranda-Pered 2016). Nevertheless, there are still rogue cosmetics manufacturers who violate this standard.

Pb is a chemical element with an atomic number of 82 and belongs to the heavy metal group with electron configurations of [Xe] 4f145d106s26p2 (Boldyrev et.al, 2018). The physical properties of Pb are soft, malleable, and has a low melting point. Pb is an abundant heavy metal, however its toxic effects can cause environmental and health problems (Tiwari, Tripathi & Tiwari, 2013). These harmful substances can affect the human reproductive system, nerves, hematopoietic, liver and kidney of humans and also cause low birth weight and changes in pregnancy, breastfeeding and menopause (Azeez et al., 2013). On the other hand, Cd is a chemical element that has an atomic number of 48 and belongs to the group of heavy silvery-white metals, with the electron configurations of [Kr] 4d105s2 (Sharma, Rawal, & Mathew, 2015). Sources of Cd come from industrial alloys, pesticides, Zn purification, etc. (Istarani & Pandebesie, 2014). Lower levels of Cd consumption can lead to a buildup of metal in the kidneys which brings the possibilities in damaging kidney and interfere with the body's metabolism (Bernard, 2008).

One of the cosmetic products that generally used is cream. A cream is a mixture of chemicals that are semi-solid in the form of an emulsion. While the whitening cream is a cream that useful to whiten the skin (Arbab & Eltahir, 2010). Skin whitening cream offers two benefits, to brighten skin color by removing or reducing the color of existing melanin (Mustarichie & Gozali, 2019); and to inhibit the formation of new melanin. The whitening cream contains various ingredients. Several of them are heavy metals such as Pb and Cd. Therefore, the purpose of this study was to determine the levels of Pb and Cd concentration in the face whitening creams that are sold in store around Sleman, Yogyakarta using AAS analysis. The AAS is used to determine the elements in a test sample in the form of a solution (Suvardhan et.al, 2004). AAS is a quantitative analysis method of elements that are very widely used, in various fields because the procedure is selective, specific, the cost of analysis is relatively cheap, high sensitivity (ppm-pb) that can easily create a matrix that conforms to standards (Okereke et. all, 2015).

2. RESEARCH METHOD

This research was conducted at the Chemistry laboratory of Faculty of Mathematics and Natural Sciences, Universitas Negeri Yogyakarta on Thursday, November 28 until Monday, December 2nd, 2019 to seek the concentration of Pb and Cd in the skin whitening creams. The analysis carried out by AAS (Lakshmi, Rajendran, & Ezhilarasan, 2015). The tools that used are AAS instrument, electrical balanced, beaker glass, erlenmeyer, volumetric flask, volume pipette, stirrer, funnel, hotplate, and filter paper. The materials that used are nitric acid, hydrogen peroxide, distilled water, and the 5 whitening creams as samples. These 5 samples of whitening creams were taken randomly from the population at a price range from IDR 10.000, - until IDR 100.000, - that saled at Sleman, Yogyakarta.

The preparation of the sample using wet digestion methods. The sample is weighed as much as 1 gram, then put into a 250 mL glass beaker. Into a glass beaker containing 1 gram of whitening cream was added nitric acid pro analyst as much as 15 mL drop by drop while heated over a hotplate at a temperature of about 100°C. The heating is done until the disappearance of brown smoke. After that, pro analysts a total of 5 mL was added drop by drop and heated to a temperature of about 100°C. Destruction process stopped when the solution has become clearer from the beginning. The solution was stand alone until cool and after it cool, then filtered using filter paper. In order to analyse using AAS, the solution was diluted 10 times. Dilution is done by taking a 1 mL solution that was destructed into a 10 mL of volumetric flask and the distilled water was poured until it reached 10 mL. The solution was diluted inserted into the vial and proceed with the analysis using AAS with concern of Pb and Cd metal. The output from the AAS was the information about concentration and absorbantion of Pb and Cd. After that, the amount of Pb and Cd in the whitening cream samples were calculated using the following equation.

Content of Pb/Cd (
$$\frac{\mu g}{g}$$
) = $\frac{c \left(\frac{\mu g}{mL}\right)}{B(g)} \times F(mL)$

With: C = metal concentration in the sample from the calibration curve F = sample dilution factor

B = sample weight of the test solution

3. **RESULTS AND DISCUSSION**

In this section, it is explained the results of research and at the same time is given the comprehensive discussion.

3.1 Result

The findings on AAS analysis for each samples of whitening creams with regards of Pb and Cd concentrations were presented in the Table 1.

Samples	Amount of Heavy Metal in the Samples		
	Pb	Cd	
Α	-0,729	1,199	
В	0,017	1,274	
С	1,082	1,254	
D	1,242	1,215	
Е	-0,409	1,232	

Table 1. The amount of Pb and Cd in the Whitening Cream Sample

Examining the data on Table 1, it is indicated that the highest amount of Pb metal contains in the sample D. Whereas for the Cd metal, the highest amount was containing in the sample C. As an opposite, the sample A signified the smallest amount of Pb and Cd metal.

3.2 Discussion

In this research, the determination of the metal content of Pb and Cd in the whitening creams using a mixture of HNO₃ and H₂O₂ as a solvent in the ratio of 3: 1 to produce the best recovery when compared with other acid mixtures such as HNO₃ - HCl 3: 1 and HNO₃ - HClO₄ 3: 1 (Demirel, 2008). Before the samples was analysed using AAS, the sample have been prepared through desctruction technique. Destruction is carried out using nitric acid to break the bonds between organic compounds and metal compounds to be analyzed. Wet destruction can be used to determine elements with very low concentrations. Wet destruction method is also carried out with the help of heat which aims to accelerate the oxidation process and accelerate the process of breaking the bonds of complex compounds between Pb and Cd with organic compounds in facial whitening creams (Anggraeni, Yuliantini, & Rahmawati, 2018).

In the process of destruction, the organic materials are oxidized completely by nitric acid, so that it will emerge brown gas bubbles. These brown gas bubbles are NO₂ gas resulting from the destruction process using nitric acid. The reactions that occur between organic material and HNO₃ as follows:

 $Metal-(CH_2O)_x + HNO_3 \rightarrow Metal-(NO_3)_x(aq) + CO_2(g) + NO(g) + H_2O$

 $2NO(g) + O_2 \rightarrow 2NO_2(g)$

The reactions that occur after H2O2 was added are as follows:

 $2H_2O_2(l) \rightarrow 2H_2O(aq) + O_2(g)$

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 $2NO_2(g) + H_2O \rightarrow HNO_3(aq) + HNO_2(aq)$ $2HNO_2(aq) \rightarrow H_2O(aq) + NO_2(g) + NO(g)$

The NO₂ gas that produced from aforementioned reactions will react with H₂O due to the addition of H₂O₂. At the time of addition of H₂O₂, it will decompose into H₂O and O₂. Then HNO₃ destroys the remaining organic materials, while HNO₂ will break down into NO₂ and NO gases. This will keep repeating during the destruction process, then it will end after all organic materials have been decomposed.

Based on the findings on Table 1, Pb concentrations in each sample A to sample E can be obtained respectively -0.0728 ppm, 0.0017 ppm, 0.1082 ppm, 0.1242 ppm, and -0.0409 ppm. Whereas for the Cd cocentrations were 0.1199 ppm, 0.1274 ppm, 0.1254 ppm, 0.1215 ppm and 0.1232 ppm for sample A until sample E respectively. According to the BPOM RI (2014), the calculation of Pb and Cd content is using the following formula:

Levels of Pb or Cd $\left(\frac{\mu g}{g}\right) = \frac{C\left(\frac{\mu g}{mL}\right)}{B(g)} \times F(mL)$ (Martines, Latief, & Rahman, 2018)

Based on aforementioned formula, "C" shows the metal concentration in the sample from the calibration curve that obtained after the sample is analyzed using AAS. The "F" is the sample dilution factor, in this study using 10 times of the dilution. While "B" shows the sample weight of the test solution, in this study the sample has a weight of 1 gram. Therefore, using those formula, the Pb levels in each sample A through sample E were found to be -0.728 μ g/mL, 0.017 μ g/mL, 1,082 μ g/mL, 1,242 μ g/mL, and -0.409 μ g/mL, 1,082 μ g/mL, 1,242 μ g/mL, and -0.409 μ g/mL, 1,082 μ g/mL, 1,242 μ g/mL, 1,254 μ g/mL, 1,215 μ g/mL and 1,232 μ g/mL respectively.

According to BPOM, the Pb level threshold is 20 ppm. Samples can be said to have met BPOM requirements if the Pb level in the sample is less than 20 ppm. In sample A and sample E, the Pb level was obtained a negative value, it can be said that samples A and E did not contain Pb or the SSA tool did not detect Pb. Therefore, samples A and E have fulfilled the requirements set by BPOM. While samples B, C, and D contain Pb metal, however the amount is less than 20 ppm, so it is indicated that samples B, C, and D have met the requirements determined by BPOM. As for Cd metal content, BPOM provides a maximum standard of Cd metal concentration in cosmetics is 5 ppm. When compared with the Cd threshold value, the Cd content in the whitening cream is below the threshold value, so that the five samples were safe to be used since it fulfils the BPOM standards.

The Pb in cosmetics is impurities in the basic ingredients of cosmetics. The basic ingredients of cosmetics such as beewax naturally contain Pb <10 ppm, dyes such as iron oxide contain Cd <1 ppm and Pb <10 ppm (Rowe, 2009). Heavy metals that accumulate in the body over a period of time can cause various health problems such as developmental and neurological disorders, cardiovascular disease, immune system disorders, digestive disorders, kidney problems, headaches, lung disorders, skin, and soft tissues, hair loss and cancer. A cosmetic can be said to be safe if it meets the maximum amount of Pb content in accordance with existing requirements. The maximum amount of Pb content in some countries is set at 20 ppm and is not specific to other heavy metals (Fernier, 2001).

The content of a heavy metal in cosmetics has side effects if used in excessive levels because the heavy metal will penetrate and then absorbed by the skin. Heavy metals that enter the bloodstream will cause the health problems. The public needs to be smart and careful in choosing cosmetics since it may offers endanger the health of the community (F. Fatmawati, 2017).

4. CONCLUSION

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Based on the results of this research, the samples of whitening cream that used in this research contain heavy metal of Pb and Cd. With the specific, in the sample A contains of -0.729 ppm Pb and 1,199 ppm Cd; sample B covers 0,017 ppm Pb and 1,274 ppm Cd; in the sample C consists of 1,082 ppm Pb and 1,254 ppm Cd; in the sample D contains a total of 1.242 ppm Pb and 1.215 ppm Cd; and in the sample E consists of -0.409 Pb and 1.232 ppm Cd. These five samples were safe to be used since it fulfils the BPOM standards. For further research, it suggested to identify another heavy metal component in the face whitening cream product, such as; arsenic, or chromium. Still, an effort should be made in order to tell the customers about the harmful effects of over consumption of the face whitening cream with heavy metal acumulations in the body.

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