The Determination of Heavy Metals Level: Lead in Cosmetic Soap Preparation by Atomic Absorption Spectrophotometer (AAS)

S R N Endah1*, S I Surantaatmadja2

1Department of Pharmacy, Perjuangan University, Tasikmalaya, Indonesia
2Department of Pharmacy, Bandung Institute of Technology, Bandung, Indonesia

*srierezekine@gmail.com

Abstract. Nowadays, the use of cosmetics are increase. Soap is one of common cosmetics preparation used for body or face. Cosmetics soap must be safe and must not contain hazardous substances such as heavy metals. Heavy metals contained in cosmetics are generally impurities on cosmetic ingredients. Cosmetics soaps can be contaminated by heavy metals such as lead. This study intended to determine lead concentration commercial cosmetics soaps in Ciamis. Sample preparation was done by using the wet destruction using HNO3 : H2O2 (3:1). Lead was analyzed using Atomic Absorption Spectrophotometer (AAS) at the specific wavelength respectively 228.8. The results showed, just one sample that contain exceed levels of lead and 9 samples are meet the requirements.

1. Introduction
Every woman want to always look beautiful. This desire can be realized by using various kinds of cosmetics. According to the Minister of Health of the Republic of Indonesia No. 445 / Menkes / Permenkes / 1998 cosmetics are preparations or alloys of materials that are ready to be used on the outside of the body (epidermis, hair, nails, lips, and external genital organs), teeth, and oral cavity for cleanliness, increase attractiveness, change appearance, protect it to remain in good condition, improve body odor but not intended to treat or cure an illness. [1]

Various kinds of cosmetics such as soap, cream, powder, lipstick and various other cosmetics can make the face look more beautiful. However, many women do not realize that among the beauty products they usually use, they may contain hazardous substances such as heavy metals [2]. As one of the most commonly used cosmetics is soap. The use of soap, both soap for face and bath soap is used almost every day with a relatively continuous time. Heavy metals contained in cosmetics are generally impurities (impurities) in the basic ingredients of making cosmetics. The risk of this heavy metal being swallowed (contamination from the hands) or inhalation allows other health problems. Heavy metals that need to be watched are often contained in lead. [3]

Lead is a type of metal that has a bluish gray color that is shiny and easily purified from mining. Lead is easy to form, has active chemical properties, so it can be used to coat the metal so that it does not...
arise. This metal belongs to group IV-A metals in the Periodic Table of chemical elements. Lead is a metal that gets attention because it is toxic through the consumption of food, drink, air, water, and lead contaminated dust. Lead enters the body through the oral route, through food, drinks, breathing, skin contact, contact through the eyes, and through parenteral. [4]

Determination of heavy metals in cosmetics can be done by wet or dry digestion as measured by Atomic Absorption Spectrophotometer [5][6]. In previous studies, in India the determination of lead in cosmetics products using samples of soap, face cream, shampoo, shaving cream and powder. Sample preparation is done by wet digestion and measured by Atomic Absorption Spectrophotometer[7]. This study aims to identify and determine lead levels contained in cosmetics soaps by using experimental research methods, namely the determination of the levels of heavy metals lead in cosmetic soap preparation using an Atomic Absorption Spectrophotometer instrument.

2. Experimental and Method

2.1. Instruments

The tools used Atomic Absorption Spectrophotometry, hollow cathode lamp for lead metals, destruction flask, heating mantle, 35 mL SPD cap vial, 1.0 mL, 2.0 mL, 5.0 mL, 10.0 mL volume pipette, 50.0 mL and 100.0 mL measured flask, and Mettler Toledo Dragon 204 analytical scale.

2.2. Material

The ingredients are Pb Standard solution 1000 mg / L (Merck), nitric acid 65% (Merck), hydrogen peroxide 30% (Merck), aquabidest, soap sample obtained in the Ciamis area.

2.3. Experiments

Development of a method of analyzing the determination of lead in soap begins with the optimization of the Atomic Absorption Spectrophotometer (AAS) tool. After obtaining the optimum tool conditions, then the optimization of the wet destruction process with a destructive tool is carried out which includes the use of various reagents as digesters. After obtaining the optimum digestion tool and process, verification of the method of determining lead with AAS was carried out which included linearity test, detection limit, quantification limit, precision and accuracy[8]. Stages in the linearity test include the manufacture of intermediate standard solutions and work standard solutions for the manufacture of calibration curves. Detection limits and tool quantization limits are determined statistically from the linear regression equation obtained from the calibration curve. Precision and accuracy are carried out by adding Lead (Pb) standards to the sample. At this stage begins with the preparation of soap samples by wet destruction with the known levels of lead. Determination of lead metals in several soap samples is carried out using verified methods. Sample preparation using wet destruction method using a mixture of 65% nitric acid and 30% hydrogen peroxide. The destruction is done with 15 ml of nitric acid as much as 15 ml added to the destructive flask and while heated at a temperature of about 100°C. This process is carried out until the loss of smoke is brown. After that the solution is added with 30% hydrogen peroxide as much as 5 ml while heating at a temperature of about 100°C. The destruction process is stopped until the clear solution indicates that the destruction process is complete. After the destruction process is complete, the solution is left to cool, then the solution is put into a 50 ml volumetric flask and add aquabides to the measuring flask, then the solution is homogenized. Then filtered using filter paper and put in a vial and measured by AAS. The sample digestion was carried out twice repetition.

3. Result and Discussion

After the conditions of AAS and destruction have been optimum, it can be continued to verify the method including linearity, detection limits, quantity limits, accuracy and precision. Determination of linearity is done by plotting the instrument response which is expressed by the measured absorption / absorbance value, with the concentration of Pb standard solutions consisting of 5 levels of
concentration. Each standard concentration is injected 3 times each. Then the calibration curve is obtained and the correlation parameter (r) and the regression function coefficient (Vx0) are determined.

In Figure 1 it can be seen that the linear regression equation Lead (Pb) is \( y = 0.0125x + 0.0014 \) with the correlation coefficient \( r = 0.9998 \). Furthermore, the linearity test of the calibration curve is carried out by calculating all linear regression parameters calculated by the statistical equation.

Table 1. Linear Regression Parameters of Lead Calibration Curves

| Parameter                                | Regresi Linier                        |
|------------------------------------------|---------------------------------------|
| Regression equation                      | \( y = 0.125x + 0.0014 \)            |
| Slope (b)                                | 0.125                                 |
| Intersect with the y-axis line (a)       | 0.0014                                |
| X average (ppm)                          | 0.00000007                            |
| Sy/x (residual standard)                 | 0.0010075                             |
| \( (Sy/x)/b \)                           | 0.0805978                             |
| \( V_{x0} \) /coefficient of variance regression (%) | 2.1981209                            |
| r (correlation coefficient)              | 0.9998                                |
| LOD/Limit of Detection (ppm)             | 0.242                                 |
| LOQ/Limit of Quantity (ppm)              | 0.806                                 |

Precision is a measure of the repeatability of the analytical method and expressed as relative standard simpagan (SBR) or coefficient of variation (KV). Precision tests are carried out with a soap matrix to see the effect of the carrier matrix on precision results. Precision is done with 6 repetitions with the addition of certain concentrations of metal that will be analyzed and injected 3 times each. Precision testing is carried out and the relative standard deviation calculated must meet the acceptability requirement which is <2%.

Acceptance requirements are SBR <0.67 KV Horwitz. Precision results of metal Pb in table 2 above obtained% SBR respectively were 0.45%, 0.78% and 0.75% entirely less than 0.67 KV Horwitz. Based on Horwitz's trumpet theory, the relative standard deviation of a method will increase and decrease concentration. If the relative standard deviation value of the experiment is compared to the
relative standard deviation calculated based on the Horwitz trumpet equation, HORWITZ RATIO or HORRAT will be obtained. HORRAT ≤ 2 indicates that the analytical method has adequate precision. From the results of precision testing on metal Pb it can be seen that the resulting coefficient of variation meets the KV requirements of Horwitz trumpet theory and has a HORRAT ≤ 2, so it is said that the method used meets the requirements of precision.

Table 2. Lead (Pb) Precision In Cosmetic Soap

| No | Concentration (µg/g) | day-1 | day-2 | day-3 |
|----|---------------------|-------|-------|-------|
| 1  | 54,4                | 54,4  | 58,4  |
| 2  | 58,4                | 58,4  | 62,4  |
| 3  | 62,4                | 58,4  | 62,4  |
| 4  | 58,4                | 54,4  | 58,4  |
| 5  | 66,4                | 58,4  | 66,4  |
| 6  | 54,4                | 54,4  | 58,4  |

Rata – rata 59,06 59,07 60,4
SB 0,26 0,44 0,43
SBR (%) 0,45 0,78 0,75
KV Horwitz 24,64 24,65 24,64
0,67 KV 16,43 16,44 16,43
HORRAT 0,03 0,05 0,05

Accuracy test on soap is carried out by standard addition method, by adding the standard with known concentration into soap and obtaining the following accuracy test results.

Table 3. Accuracy of Lead (Pb) in cosmetic soap

| No | Analyte Concentration without spike (µg/g) | Analyte Concentration with spike (µg/g) | Obtained Analyte Concentration (µg/g) | Added Analyte Concentration (µg/g) | Recovery (%) |
|----|-------------------------------------------|----------------------------------------|--------------------------------------|-----------------------------------|--------------|
| 1  | 134,4                                     | 186,4                                  | 52                                   | 50                                | 104          |
| 2  | 134,4                                     | 186,4                                  | 52                                   | 50                                | 104          |
| 3  | 134,4                                     | 182,4                                  | 48                                   | 50                                | 96           |
| 4  | 134,4                                     | 230,4                                  | 96                                   | 100                               | 96           |
| 5  | 134,4                                     | 234,4                                  | 100                                  | 100                               | 100          |
| 6  | 134,4                                     | 238,4                                  | 104                                  | 100                               | 104          |
| 7  | 134,4                                     | 410,4                                  | 276                                  | 250                               | 110          |
| 8  | 134,4                                     | 394,4                                  | 260                                  | 250                               | 104          |
| 9  | 134,4                                     | 402,4                                  | 268                                  | 250                               | 107          |

Average of Recovery (%) 102,78

Accuracy of Lead is expressed by percent recovery which is calculated by recovery calculation. From tables 3 above recovered Pb in soap each between 96 - 110%. This fulfills the acceptability requirements for accuracy that is in the range 80 - 120% Specificity test was not carried out because the hollow cathode lamp used in atomic absorption spectrophotometry was specific to each type of metal analyzed.
Determination of Pb and Cd metal content from soap samples using a validated method.

Table 4. Concentration of Lead (Pb) in Cosmetic Soap from Several Markets in Ciamis Area

| Sample  | Concentration of Pb in Cosmetic Soap (µg/g) | Konsentrasi rata – rata (µg/g) |
|---------|------------------------------------------|-------------------------------|
| Soap 1  | 22.4                                     | 22.4                          |
| Soap 2  | 6.4                                      | 6.4                           |
| Soap 3  | 10.4                                     | 10.4                          |
| Soap 4  | 6.4                                      | 6.4                           |
| Soap 5  | 18.4                                     | 18.4                          |
| Soap 6  | 14.4                                     | 14.4                          |
| Soap 7  | 10.4                                     | 10.4                          |
| Soap 8  | 18.4                                     | 18.4                          |
| Soap 9  | 18.4                                     | 18.4                          |
| Soap 10 | 6.4                                      | 6.4                           |

Requirements for lead metal according to the Regulation of the Head of BPOM RI Number HK 03.1.23.07.11.6662 is < 20 µg / g. The soap sample 1 exceeds the regulatory limit of lead metal which is 22.4 µg / g. It can be caused by the exposure by lead metal from the equipment during the soap making process or environment during the production process. For other samples, lead metal were detected but still below the regulatory limits.

4. Conclusion

Based on the research that has been carried out the method of determining Lead metal (Pb) in cosmetic soap using an Atomic Absorption Spectrophotometer analysis technique has been obtained. The results of the validation of the analysis method show the following results the linear regression equation is \( y = 0.0125x + 0.0014 \) with a correlation coefficient of \( r = 0.9998 \), detection limits and quantitation limits are 0.242 ppm and 0.806 ppm Precision is relative standard deviation 0.20% and recovery 96 - 110%. Based on the results of the determination of Lead (Pb) from samples of cosmetics soaps traded in the district of Ciamis on some soaps there are several contents of Lead (Pb). Soap sample 1 exceeds the regulatory limit of lead metal which is 22.4 µg / g.

5. References

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