Original Research Article: Analysis of the Heavy Metal Content of Coloring Paste "Silver-Man Beggar" in Surakarta, Indonesia

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ABSTRACT

In late December 2019, a mysterious pneumonia outbreak characterized by fever, dry cough, and fatigue, and occasional gastrointestinal symptoms occurred in Wuhan, Hubei, China. The existence of a pandemic causes reduced social welfare, income to termination of employment. With uncertain conditions causing changes in people's lifestyles, one of them is becoming a silver human beggar. In Indonesia, there have been numerous silverman beggar phenomena since 2020. The Silver Man is a beggar who intentionally paints his body in silver. In the action, the silver man adds cooking oil to a coloring paste mixture of iron paint or screen printing paint to make it appear glossy. This coloring substance is typically applied all over the body and lasts for at least 12 hours. The use of coloring paste that is contradictory with its designation will result in a variety of health issues. This is because the coloring substance contains several heavy metals. The heavy metals mercury, lead, and cadmium have been detected in five areas in the Surakarta region. This heavy metal content exceeds the safety limit for heavy metals on the epidermis, which is less than 5 mg/Kg. This may result in irritation, anemia, kidney problems, tissue disorders, cancer, and even mortality. Thus, it is necessary to seek out alternatives to reduce exposure to heavy metals.

Introduction

In late December 2019, a mysterious pneumonia outbreak characterized by fever, dry cough, and fatigue, and occasional gastrointestinal symptoms occurred in Wuhan, Hubei, China [1]. This outbreak was later referred to as Covid-19 which eventually became a global pandemic [2]. The Covid-19 pandemic has caused very significant social changes for the Indonesian people. The existence of a pandemic causes reduced social welfare, income to termination of employment [3,4]. While social welfare is something that everyone or every group wants to achieve, social welfare is said to have been achieved when the necessities of life have been met, both basic needs and secondary needs. There are still many people who find it difficult to meet their daily needs [5]. With uncertain conditions causing changes in people's

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lifestyles, one of them is becoming a silver human beggar (Figure 1).

Figure 1: Illustration of Indonesian Silver-Man Beggar [21]

At first the silver human phenomenon was used to raise aid or charity for victims of natural disasters. With this pandemic, many people, especially those who are still teenagers, are busking at traffic lights by painting their bodies with silver paint [6,7]. Silver coloring paste is usually made from clothes printing paint or iron paint which is metallic silver and then mixed with palm oil and baby oil to make it more shiny. Clothes printing paint and iron paint may contains many heavy metals including lead (Pb), cadmium (Cd) and mercury (Hg) [8-10]. Lead poisoning can cause anemia, hypertension, kidney, and nerve disorders and at certain doses cause death [11-13]. Cadmium poisoning can cause fever, chills, muscle damage, and respiratory problems [14,15]. Meanwhile, mercury poisoning can cause tremors, insomnia, memory loss, nervous disorders, headaches, and motor dysfunction [16,17]. The levels of heavy metals in paint can be determined using atomic absorption spectroscopy [18-20]. In this study, we will develop a method and determine the levels of heavy metals (lead, cadmium and mercury) in paints used by silver man in central java, Indonesia. The purpose of this study is to educate the public about the dangers of using coloring paste or paint that is not in accordance with its designation.

Experimental

Materials and Methods

While the materials used were silver human paint samples obtained from 5 different cities in Surakarta district, Central Java, Indonesia. Nitric acid and perchloric acid (Merck, Germany) were used for digestion, demineralized water, Pb standard solution, Cd standard solution, and Hg standard solution (Merck, Germany). The tools used in this experiment included Atomic Absorption Spectroscopy (AAS) equipped with hydride vapor generator (HVG) Shimadzu AA-7000 (Shimadzu, Japan), Magnetic stirrer (Thermo Scientific. USA). Laboratory glassware such as beaker glass, Erlenmeyer for digestion, and measuring flask (Iwaki Pyrex, Japan).

Methods

Sample digestion and analysis

The digestion was carried out using the wet digestion method using strong acid, as much as 1 gram of coloring paste sample was put in a Erlenmeyer, then 70 mL concentrated nitric acid followed by 30 mL perchloric acid were added until the color of the solution was clear [22,23]. The solution is accommodated in a suitable measuring flask. The solution were analyzed with an atomic absorption spectrophotometer.

Method Validation

Method validation is used to ensure whether the method used is valid and can be used for metal sample analysis. The validation parameters set include Linearity, Limit of Detection (LOD), Limit of Quantitation (LOQ), Accuracy, and Repeatability [24].

Linearity

Seven series of standards were made with a range between 0.1 µg/mL and 40 µg/mL from standard Pb, Cd, and Hg spiked on the sample, and then analyzed with an atomic absorption spectrophotometer. Thereafter, the results are calculated for linearity, CV, LOD, and LOQ.

Accuracy

Three series of assays were made by adding standard to each sample with levels of 80, 100, and 120% of the metal content of the samples, and then analyzed with an atomic absorption spectrophotometer. After that, the results are calculated as a percentage of recovery and the CV.

Intra Day Precision

Seven series of the same concentration sample content were made, and then analyzed with an atomic absorption spectrophotometer with the appropriate wavelength for each metal. Furthermore, the results are calculated for the CV.

Results and Discussion

The sample was obtained from a silver man from five different cities including Surakarta, Sukoharjo, Karanganyar, Klaten, and Sragen. The sample was then subjected to an analysis of the determination of Mercury (Hg), Lead (Pb), and Cadmium (Cd) metal levels, and then validation of the analytical method was carried out with the parameters Linearity, LOD, LOQ, Intra Day Precision, and Accuracy. The results of the method validation test are listed in Table 1.

The silverman beggar is a new phenomenon whose number is increasing as a result of the COVID-19 pandemic. Silverman is a beggar who paint his body with silver paint or coloring. This silver coloring paste comes from clothing coloring paste or screen printing which is combined with baby oil, palm oil, and dish soap so that it sticks and is moist on the skin. The use of this paint is directly applied to the surface of the skin and continues to be used from morning to night. In this study, an analysis of the heavy metal content of the silver coloring paste used by silver people in the city of Surakarta District was carried out. Samples were obtained from 5 cities in the district of Surakarta. Analysis of heavy metal content was carried out using the atomic absorption spectroscopy method with 3 (three) heavy metal liquid standards, namely Mercury (Hg), Cadmium (Cd), and Lead (Pb). The selection of these metals is based on the level of metal hazard to humans and BPOM (Indonesian Food and Drugs Administration) regulations regarding metal limits in cosmetic preparations [25]. Silver coloring paste is equated as a cosmetic because its use is applied to the surface of the body for 12 hours or more.

Determination for heavy metals is initially carried out by validating the analytical method. Validation of analytical methods includes linearity, repeatability, accuracy, Limit of Detection (LOD), and Limit of Quantitation (LOQ). The linearity results are listed in Table 1, these results indicate a good methods for response to changes in sample concentration as evidenced by the value of r >0.98, and then the precision parameter (Table 2) shows good repeatability with an RSD value of less than 5.0%. This shows that the analytical method used is quite consistent and robust when used for simultaneous measurements in the same time period. Thereafter, related to the accuracy results, the recovery is obtained (Table 3) with a range of 80-120% and RSD <5%. This result ensures that the method used is close to the actual reference standard value. Meanwhile, for LOD and LOQ (Table 4), the results were quite good.

Table 1: Linearity of heavy metals

Mercury (Hg)	Lead (Pb)	Cadmium (Cd)
y = 0.0184x + 0,027	y = 0.011x + 0.0201	y = 0.0666x + 0.023
R^2 = 0.9844	R^2 = 0.9994	R^2 = 0.9871

Table 2: Intraday CV (%)

Mercury (Hg)	Lead (Pb)	Cadmium (Cd)
4.73	2.02	1.61

Table 3: %Recovery of heavy metals

Mercury (Hg)	Lead (Pb)	Cadmium (Cd)
90.1	103.5	107.2

Table 4: LOD and LOQ of heavy metals (mg/L)

	Mercury (Hg)	Lead (Pb)	Cadmium (Cd)
LOD	0.0351	0.0121	0.0312
LOQ	0.117	0.0403	0.104

Table 5: Heavy metals content

Region	Mercury (Hg) (mg/Kg)	Lead (Pb) (mg/Kg)	Cadmium (Cd) (mg/Kg)
Karanganyar	4.84	8.26	ND
Klaten	7.01	14.63	0.035
Sukoharjo	6.41	14.26	ND
Surakarta	10.76	16.35	0.135
Sragen	6.85	6.08	0.045

Analysis of heavy metals in coloring paste samples was carried out by digesting paste samples using a mixture of HNO_3 and $HClO_4$ (70:30). Destruction is carried out to remove organic components in the sample that can interfere with readings with AAS. The use of this acid combination is intended to increase the efficiency of wet digestion. A total of 1 gram of coloring paste sample was destroyed with 100 mL of a mixture of HNO_3 and $HClO_4$ (70:30). Optimal conditions to obtain a clear solution in this experiment is at 150 ^oC for 120 minutes, and then an analysis was carried out using AAS, as presented in Table 5. These results indicate that the levels of mercury and lead exceed the limits permitted by BPOM (Indonesian Food and Drug Administration) or not more than 5 mg/Kg. The Surakarta region had elevated mercury and lead concentrations. This is a result of extended exposure in the city combined with air pollution, which has led to extremely severe metal contamination. In addition, the Sukoharjo and Klaten regions are also industrial hubs with significant pollution from factories.

Continuous exposure mercury to the skin can cause skin irritation, skin discoloration, cause rashes and blotchy spots, and give skin a grayish color and under certain conditions can penetrate the skin causing cancer. While exposure to lead over a long period of time can cause even in normal-appearing skin, the hydration level and elasticity decreases in lead-intoxicated patients [26].

Prolonged exposure to cadmium causes hyperkeratosis and acanthosis, accompanied by occasional ulcerative changes, and an increase of the mitotic index of the skin cells [14]. The use of silver coloring paste on the body for a long time can increase the risk of skin problems and there is a possibility of heavy metals entering the bloodstream so that they can cause more complex health problems. Therefore, it is necessary to educate silverman beggar so they can find other alternatives in carrying out these activities or reduce exposure to the skin by changing to using costumes or other alternatives.

Conclusion

Long-term occurrence of the silver-man beggar phenomenon in the Surakarta region due to Covid-19 will result in severe health issues. This is because the concentration of mercury and lead exceeds the safe limit for

topical application. This necessitates a reduction in its usage and the search for safer alternatives.

Orcid

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