Chemical Analysis of Heavy Metals in Organic, Counterfeit and Local Brand Lipsticks Using Hydride Vapor Generation Technique –Atomic Absorption Spectroscopy

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ABSTRACT

Cosmetics are noted for the most part as significant in liberating heavy metals into the human biological system. Heavy metal impurities in cosmetic products, whether it is an organic, a local brand or counterfeit, are unavoidable because of the ubiquitous nature of these elements. Moreover, it has been a subject of research that high doses of heavy metals can be fatal, and that even long-term exposure to low levels of heavy metals can cause certain types cancer and health risks. In this study, researchers aim to evaluate the concentration of heavy metals present in organic, counterfeit, and local brand lipstick. Carefully selected organic, local and counterfeit brand lipsticks procured at different prices were analyzed through acid digestion and quantitation by Hydride Vapor Generation Technique - Atomic Absorption Spectrophotometer (AAS). Based on the results obtained, concentration of heavy metals yielded in Samples A, B and C passed the permissible limits based on the ASEAN Guidelines on Limits of Contaminants for Cosmetics. Sample A (Organic) has the least traces of heavy metals, and Sample D (Counterfeit) contained the highest level of heavy metals among the four samples. Researchers would like to elevate the responsiveness of private and government health sectors as cosmetic products must be thoroughly evaluated for their safety prior to marketing. Moreover, consumers must be cautious in selecting the products they use, and must be aware of the health risks they may pose.

Keywords: Heavy Metals, Cosmetics, Counterfeit Lipstick, Hydride Vapor Generation Technique, Spectrophotometer

INTRODUCTION

As early as 4000 BCE, cosmetics had been an essential part of the human civilization. Egyptians, for example, believed that maintaining one's hygiene bestow them a way to afterlife. Chinese, on the other hand, used gum Arabic, gelatin, beeswax, and egg to stain their fingernails as a depiction of social class during the Chou dynasty. Dyed red hair, in addition, comes into fashion in Elizabethan England. Women even wear egg whites over their faces to create the appearance of a paler complexion during the Middle Ages (Chaudhri & Jain, 2009).

Over the recent years, the global cosmetic market still is increasing at a tremendous rate driven by the consumers' demand. Cosmetics enhance physical features and help build confidence among users in this day and age. According to 2011 Household Expenditure Survey, Australians spend around $4.5 billion on cosmetic products every year. In the Philippines, Kantar Worldpanel (2017), which tracks in-home shopping behavior of 3,000 homes in urban and rural areas, revealed make-ups and skincare essentials dominated the Filipinos' buying habits (Chaudhri & Jain, 2009).

The United States Food and Drug Administration (US FDA) originally does not have apparent guidelines on heavy metal contamination in cosmetics. Formerly, only color additives are being regulated. In October 2007, Campaign for Safe Cosmetics conducted a research conveying that 33 popular lipstick samples yielded positive for lead contamination. Philippine FDA further analyzed Lead, Arsenic and Mercury in 36 lipstick products which were not FDA-notified using the Field X-ray Fluorescence (XRF) instrument and the ASEAN Harmonized Laboratory method in February 2014. The study indicated that 55.5% of the samples actually contained alarming levels of Arsenic and Lead. These findings caught the attention of the health sectors and administration, and thus, they have decided to set a 20 ppm lead contamination limit for cosmetic lip products under the Food, Drug and Cosmetic Act (Järup, 2013).

Heavy metals occur naturally, and are noted for the most part as significant in liberating heavy metals into the human biological system. While only trace amounts of heavy metals are ingested from lipstick, it accumulates in the body. These dangerous heavy metal impurities include Arsenic, Cadmium, Lead, and Mercury (Al-Saleh, Al-Enazi & Shinwari, 2009). Exposure to Cadmium may be life-threatening in high contamination causing kidney failure, lung cancer, and Itai-Itai disease which is commonly manifested by osteomalacia and osteoporosis causing skeletal damage. Metallic mercury, on the other hand, which had been previously used in ointments and creams, is now known to cause kidney damage and Minamata disease characterized by psychological and neurological symptoms. Acute Lead poisoning, in addition, causes encephalopathy and Plumbism. Arsenic exposure, also, poses health risks as severe cardiovascular and central nervous system disturbance could occur and eventually lead to death. The latest evaluation of the World Health Organization (WHO) concludes that arsenic exposure is related to lungs, kidney, bladder, and skin cancer (Järup, 2013).

Following such observations, there is an ever-increasing need to examine the concentration of heavy metals on various cosmetic products. The researchers, therefore, decided to conduct a chemical analysis of heavy metals on organic, local and counterfeit lipstick samples using Hydride Vapor Generation Technique - Atomic Absorption Spectroscopy (Chauhan, 2014).

This study aims determine the sample lipsticks contained toxic heavy metals, specifically arsenic, cadmium, lead, and mercury. Specifically the study aims to: 1) evaluate whether the heavy metal contents of four samples falls within the permissible limit in accordance with the ASEAN Guidelines on Limits of Contaminants for Cosmetics; 2.) compare the amount of heavy metal impurities between the organic, counterfeit and local brand lipstick.

MATERIALS AND METHODS

The researchers used quasi-experimental method in the study, which involves selecting groups, upon which a variable is tested, without any random pre-selection processes (Castillo, 2002). The method aimed to evaluate the amount of heavy metals present in various categories of lipsticks samples in the market. The procedures were comprised of collection, preparation and instrumentation by the use of an Atomic Absorption Spectrophotometer. Quantities of chemical elements present in samples were measured through the absorbed radiation of the chemical element of interest.

Preparation of samples and experimentation of the study was conducted at the Standard Global Services (SGS) Philippines, Inc., Makati City, Philippines. The laboratory was chosen upon recommendation of the Department of Science and Technology, Los Banos. SGS is the world's leading inspection, verification, testing and assessment company, recognized as the global benchmark for quality and integrity, and staffed by knowledgeable and experienced personnel. They also offer comprehensive range of world-leading investigation and certification based on national and international standards.

Sample of lipsticks classified as Organic with Natural Products Association Seal, and Local lipsticks, which are manufactured only in the Philippines, are procured from a shopping mall in Calamba, Laguna. Counterfeit lipsticks, whose names do not appear under the Licensed Registered Cosmetic Products of the FDA, were purchased from vendors in sidewalks. Twenty-five (25) samples of red lipsticks for each brand were purposely selected according to popularity. Popularity of chosen lipstick samples was based on a study conducted by the Polytechnic University of the Philippines on preference of students on local and international lipstick brands (Quizon, 2016). The sampling frame was limited only to brands available for selection. Popular lipstick brands that were not available at the time of procurement would have been missed.

Nitric acid, Hydrochloric acid, Hydrogen peroxide 30% v/v, 50% w/v Magnesium nitrate, deionized water, 10% w/v potassium iodide and 10 % w/v ascorbic acid were used in the study. All reagents utilized were of analytical grade and provided by the SGS Philippines, Inc.

All glassware and plastic containers used were rinsed with water and soaked in 10% v/v Nitric Acid for 24hrs, and were cleaned thoroughly with distilled water and dried in such a manner to ensure that any contamination did not occur. 25 organic lipstick samples, each containing 4g, were weighed to make a 100g sample with electrical analytical balance and will be put in a digestion flask. The procedure was repeated for both local and counterfeit brands (Belurkar & Yadawe 2017).

100g of samples was put into a digestion tube with screw cap, and 7mL of conc. nitric acid was added. Sample solution was then heated in a block heater at 60˚C for at least 3 hours. Upon completion, the cooled solution was diluted with water to volume (50mL) and was allowed to stand for 24 hours in the refrigerator. Additionally, the prepared solution was filtered using the Whatman paper No. 4 before it was subjected for instrumentation analysis (Belurkar & Yadawe, 2017).

The amount of heavy metals contamination in the lipstick samples was evaluated using the FIAS-AAS (Hydride Generation System. FIAS-AAS is a valuable analytical method in determining most metal and metalloids that offers technique with sufficient sensitivity for many applications and relatively interference free. The procedure was carried out by respectively injecting and evaluating standard calibration solution and sample solutions in the FIAS-AAS (Hydride Generation System) machine at the specified condition. The machine then generated a result measuring the absorbed radiation by the chemical element of interest which is determined from a calibration curve, obtained using standards of known concentration (Bukhari, Rehman, Rasool & Munir, 2013).

Conveyed results were recorded and plotted as the response (absorbance or peak height or area) versus concentration of each standard solution. Results were tabulated and evaluated using the One-Way Analysis of Variance. Moreover, Health Risk Exposure is also evaluated by calculating the Systemic Exposure Dose and Margin of Safety (MoS) of the heavy metals present in lipstick samples. This assessed the risk of human exposure to metals in cosmetic products, is calculated by dividing the no observed adverse effect level (NOAEL) value of the lipstick under study by its estimated systemic exposure dosage (SED) (Nnorom and Igwe, 2005).

RESULTS AND DISCUSSIONS

The main principle of this method is to quantitatively determine traces of heavy metals through the amount of absorbed light at the resonant wavelength as light passes through a cloud of atoms in a sample.

The table illustrates the result of heavy metal analysis such as lead, cadmium, arsenic and mercury in organic, local and counterfeit brands of lipstick. Results demonstrate that traces of heavy metals in Sample A, B and C are within the permissible limit, while traces of heavy metals present in sample D exceed the permissible limit. Results indicate that lipsticks containing natural ingredients have the least concentration of heavy metal impurities. It is also conveyed that not all counterfeit lipsticks contain heavy metal impurities above the permissible limit. However, the general safety of counterfeit lipsticks is not guaranteed since Sample D contains alarming amounts of heavy metal impurities.

Table 1. Traces of heavy metals on different samples of lipstick

SAMPLE	LEAD (Pb)	CADMIUM (Cd)	ARSENIC (As)	MERCURY (Hg)	LIMIT
A (Organic)	1.46 ppm	0.85ppm	0.32 ppm	0.05 ppm	Low
B (Local)	7.18 ppm	4.63 ppm	2.5 ppm	0.41 ppm	Low
C (Counterfeit)	6.54 ppm	3.27 ppm	2.89 ppm	0.53 ppm	Low
D (Counterfeit)	52.89 ppm	34.02 ppm	17.50 ppm	11.32 ppm	High

Permissible Limit: ≤1 ppm (Hg), ≤20 ppm (Pb), ≤5 ppm (As), and ≤5 ppm (Cd) (ASEAN Guidelines on Limits of Contaminants for Cosmetics, 2018)

The calculated systemic exposure dosage (μg/kg bw/day) from the lipstick products at 50% bioaccessibility is shown in Table 2. The SED of heavy metals in the sample lipsticks falls within the permissible exposure dose set by the European Food Safety Authority for Pb, Cd, As and Hg. Results demonstrated that daily use of lipstick samples exposes the consumers to low levels of heavy metal residues. Moreover, organic lipstick has the lowest value for SED among the lipsticks examined. The highest amount of systemic exposure dose that can be obtained from the samples is from lead in counterfeit lipstick.

Table 2. Evaluation of the contents of lipstick samples in accordance with permissible limits

Sample	Lead	Cadmium	Arsenic	Mercury	Exposure
A	3.3288×10^{-3}	1.938×10^{-3}	7.296×10^{-4}	1.12×10^{-4}	Low
B	0.0163704	0.0105564	5.7×10^{-3}	9.348×10^{-4}	Low
C	0.0149112	7.4556×10^{-3}	6.5892×10^{-3}	1.2084×10^{-3}	Low
D	0.1205892	0.0775656	0.0399	0.0258096	Low

Permissible exposure dose: 3.6 μg/kg bw for Pb, 0.4 μg/kg bw for Cd, 2.1 μg/kg bw/day for As, 0.6 μg/kg bw for Hg (European Food Safety Authority, 2008)

As proposed by the WHO, when the Margin of Safety of an ingredient is >100, it is considered to be safe, and if the MoS of an ingredient is <100, the ingredients is considered to have some risks. Table 3 illustrates the MoS of heavy metals from the lipstick products examined. Results conveyed that Organic Lipstick has the highest value of MoS, while Counterfeit Lipstick has the least value for margin of safety on all heavy metals analyzed. It is also notable that the calculated MoS for Lead and Cadmium in Counterfeit Lipstick are higher than that of the Local Brand. However, results demonstrated that Lead and Cadmium in Sample A were the only heavy metal impurity higher than the minimum value of 100. In addition, MoS of heavy metal contamination in a Counterfeit Lipstick <1 indicates higher risk for adverse effect.

Table 3. Comparison of heavy metals impurities from different samples of lipstick

Sample	Lead	Cadmium	Arsenic	Mercury
A	120.1634	151.59959	41.11842	87.71929
B	24.43434	9.47293	5.26316	10.69748
C	26.82547	13.43075	4.55290	8.27541
D	3.31705	1.28923	0.75188	0.38745

CONCLUSION AND RECOMMENDATION

Based on the findings of the study, the resaerchers concluded that heavy metal residues are ubiquitous in lipstick production. Additionally, Organic Lipstick has the least traces of heavy metals, indicating that lipsticks containing natural ingredients have the least concentration of heavy metal impurities. Counterfeit lipstick on the other hand, yield the highest level of heavy metals among the four samples.

On health risk assessment, the calculated SED on four samples conveyed the hypothetical amount of heavy metals that can enter the biological system upon use. Though results indicated that daily use of lipstick samples exposes the consumer to only low levels of heavy metal residues, Margin of Safety for Counterfeit lipstick is <1 indicating great risk for adverse reaction, following repeated exposure. Likewise, MoS for Local lipstick is <100 conveying an appreciable risk to the consumer. MoS values obtained for Organic lipstick is >100, suggesting that there is no toxicological concern for systemic toxicity. Therefore, the study suggested the use of technological studies in the development of a less costly but highly efficient detection, identification and quantization of heavy metals. Regular monitoring of the heavy metals present in different cosmetic products should be emphasized to avert the possible risk of heavy metal poisoning through long term oral exposure.

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