Assessment of Hg, Pb, Cd, and As in Lip Gloss Samples purchase in an open market in Enugu State. Nigeria.

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Abstract: Lip gloss (shiny lip cosmetic: a cosmetic used on the lips to make them look shiny) are a possible source of heavy metal exposure to human. Ten lip gloss sample commonly consumed in Nigeria were purchased from an open market in Enugu North local government area of Enugu State. The samples were analyzed for heavy metals content such as Mercury (Hg), Arsenic (As), Lead (Pb) and Cadmium (Cd). The Cold Vapor Atomic Absorption Spectrometric method was used for the determination of mercury, the FIAS - AAS (Hydride Generation System) at the specified conditions for arsenic. Lead and Cadmium were determined using the flame atomic absorption spectrometry (FAAS). The result from this study reveals that mercury was not detected in all the samples analyzed for heavy metals. 30% of the lip gloss samples analyzed for Pb reveal that the metal concentration was below detectable limit while 70% of the samples tested for the metal reveal an appreciable concentration with the highest value of Pb amounting to 1.81ppm, closely followed in concentration with 1.56ppm and the least concentration value amounting to 0.56ppm and 0.19ppm. Arsenic was detected in 70% (7 out the 10) samples in the range of 0.25ppm to 2.44ppm. The highest concentration value for arsenic amounted to 2.44ppm. The second highest concentration value was 1.81ppm. Cadmium was detected in 60% (six of the ten) lip gloss sample analyzed in this study. The highest concentration value for cadmium was recorded as 0.31ppm, followed by 0.30ppm. The least concentration value for cadmium was 0.02ppm, followed by 0.01ppm. Generally, the study reveals lip gloss samples showing increase in the concentration of the metals to be higher than the maximum acceptable limit for those of the Guidelines for Canadian Drinking Water Quality, the United States Food and Drug Administration and the federal Ministry of Health in Germany. The presence of these metals in the tested samples could be attributed to the fact that these metals occurs naturally in the environment and they can make their way in trace quantities into raw materials. Acceptable limits for heavy metals vary according to firstly, the subpopulation of interest (for example, children are more susceptible to heavy metal toxicity than adults and have greater exposure potential due to hand - to - mouth activity). Secondly, the amount of product used and thirdly, the site of application (for example arms versus lips). Our findings thus, call for an instant mandatory regular testing program to check metals like mercury, arsenic, lead, cadmium and other toxic metals in lip gloss products sold in our market and also to educate the masses in order to limit usage in other to protect consumer health

Key word: Lip gloss, cosmetics, heavy metal, cold vapour atomic absorption spectrometer, hydride generator system, Food and drug administration (FDA), maximum acceptable limit, digestion.

In recent years, there has been growing consumer concern that cosmetics may contain harmful levels of toxic substances. For instance, in 2007, the Campaign for Safe Cosmetics published a report drawing attention to the lead content in lipsticks and lip glosses, and in 2009 and 2011, the Food and Drug Administration (FDA) published its own findings on lead in lipsticks. The quest for beauty tends to promote the use of cosmetics by men and women in spite of the profound interest in heavy metal hazards of cosmetics [Orish and Jonathan (2013); Abdel – Fattah, and Pingitore Jr., (2009); Al – Saleh, *et. al.*, (2009); Ayenimo, *et. al.*, (2010)]. Although beauty consciousness of people in the eastern part of Nigeria has set the demand for cosmetics such as lip gloss (shiny lip cosmetic: a cosmetic used on the lips to make them look shiny) in market, especially for the teenage, young adult and children, their side effects as well as health consciousness of people has attracted clinicians and researchers to find out the probable reason behind these undesirable secondary effect produced by lip gloss. Heavy metal contamination is one of the important reasons behind the same problem. Metals like lead and cadmium are common contaminant in various cosmetic products [Nnorom, *et. al.*, (2005); Al – Saleh, *et. al.*, (2009)]. It was reported by the Centre for Science and Environment, and the Pollution Monitoring Laboratory, New Delhi that test conducted in the

United States by the Campaign for Safe Cosmetics revealed that 61% of the 33 brands of lipsticks analyzed contained lead, with levels of up to 0.65ppm. It was further reported that the United States Food and Drug Administration also found lead in all the samples of lipstick that was investigated, with levels ranging from 0.09 to 3.06 ppm and also, Health Canada found that 81% of the samples of lipstick that was investigate for lead has levels ranging from 0.079 to 0.84ppm, and that one lipstick contained 6.30 ppm. This is despite many metals being banned as intentional ingredients - Any single chemical entity or mixture used as a component in the manufacture of a cosmetic product - in cosmetics in Canada [Draft Guidance on Heavy Metal Impurities in Cosmetics (2010)]. They are not banned as product impurities since their presence as such is considered unavoidable. An impurity is a substance that is not intentionally added to a product, but rather, as a by - product of the manufacturing process formed by the breakdown of ingredients or as an environmental contaminant of raw ingredients. The latter is the case for heavy metals, as their persistence in the environment and their natural presence in rock, soil and water lead to their presence in pigments and other raw materials used in various industries, including cosmetics as reported by the Impurities of Concern in Personal Care Products (2010). Poppiti, and Charles (1994) reported that the Pigments used as ingredients in lipsticks 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. They further states that Pigments give lipstick its color and covering power. The concentration of pure pigment can vary from 1% to 10% depending on the type of product (lip gloss to a dark lipstick). The most widely used pigments are mineral (titanium and iron oxides) and organic pigments (true pigments, toners and lakes) [Tracy, 2013]. Although many studies have reported the presence of heavy metals in cosmetic products especially in lipsticks, nail polish and body cream, however data about their presence in lip gloss is scanty. Present study thus planned to assess the public health risk of heavy metals - lead, cadmium, mercury, and arsenic - from certain brands of lip gloss products sold at our local Ogbete markets and the results compared to the available standard. Also, the study is aimed to investigate if lip gloss products sold in our local store were non – complaint with this available standards since most of this products are imported from countries which may have weak regulatory inspection and screening as well as no standard conditions for manufacturing.

Materials and Methods

Ten (10) samples of lip gloss were randomly purchased in duplicates for analysis in an open market from a retails store in the Ogbete market. The Ogbete market is a stone throw to the Holy Ghost cathedral in Enugu north local government area of Enugu State, Nigeria. The details of the samples analyzed are presented in Table 2. Lip gloss was analyzed for lead, Mercury, Arsenic, and cadmium.

Sample preparation

Blank was prepared as in sample preparation but without adding the lip gloss sample. Sample preparation was carried out by accurately weighing samples to the nearest mg in duplicate, 0.15 – 0.20 g of sample was measured into a high pressure resistance 50mL quartz or TFM vessel. 3mL concentrated nitric acid and 30 % hydrogen peroxide 1mL was added by using graduated pipette. 1mL concentrated hydrochloric was added since the lip gloss contains pigments. The vessel lid was closed and Left for about 15 minutes to ensure complete reaction before subjecting to microwave digestion.

The Cold Vapor Atomic Absorption Spectrometric method for the Determination of Mercury

Samples were digested using 0.5g of analytical sample by weight. 0.5g reagent water was used for method blanks (MBKs). 1.0 mL 1% (w/v) of sodium chloride solution and 5.0mL concentrated HNO_3 was Pipette into vessel liner. The vessels were sealed, pressure relief nuts were tightened and digestion was performed. The vessel was cooled to less than 50 °C and

then they were removed to an exhausting hood and vent excess pressure slowly. Approximately 10mL reagent water and 3.5mL HCl was place in 50mL capacity polypropylene tube. The digestion solution was quantitatively transferred into the 50mL tube. The tube was Seal and then shakes vigorously. The cap was removed for approximately 5 minutes to release trapped gas from the warm solution. This was diluted to slightly less than 50 mL with reagent water. The container was resealed and cool to room temperature and then diluted to 50.0 mL with reagent water. The tube was resealed and thorough mix. The analytical solutions were taken for analysis when a clear and colorless to faintly yellow colour was observed, indicating that digestion is acceptably complete.

Digestion of samples for arsenic, lead and cadmium

The samples of lip gloss were separately emptied into clean beakers in duplicate and these were transferred into a homogenizer. It was homogenized for 10 min at 1000 rpm. 5 ml of each sample was carefully pipette into the digestion test tubes in a digestion rack and 25 ml of the digested acid (2:2:1 HNO_3: H_2SO_4: $HClO_4$) was added to each sample. This was placed on the digester inside the fume cupboard. On completion of digestion, the digested samples were allowed to cool to room temperature and made up to 50mls with distilled water. The samples were transferred into centrifuge tubes, shook in a mechanical shaker for 10 min at 1500 rpm and then centrifuged for 5 min at 5000 rpm to allow the particles to settle. 25 ml supernatant of each sample were filtered through Whatman paper no.1 into 50 mL volumetric flask and dilute to volume with deionised water transferred into pyrex vials for analysis.

Sample analysis for Lead, Arsenic, Mercury and Cadmium Determination

Standard calibration solutions was injected into the FIAS - AAS (Cold vapor Technique) for the determination of mercury, the FIAS - AAS (Hydride Generation System) at the specified conditions for the determination of arsenic, Lead and Cadmium were determined using the flame atomic absorption spectrometry (AAS). The (absorbance or peak height or area) versus concentration of each standard solution was plot in response.

Results and Discussion

The results of lip gloss samples analyzed for it heavy metal content is presented in table 2 and 3.

Table 1: Results of Hg, As, Pb and Cd in (ppm) on 10 (Ten) lip gloss

S/N	Sample	As	Hg	Pb	Cd
1.	Black Opal	0.25	ND	1.06	ND
2.	Miss Rose	ND	ND	ND	0.01
3.	African Queen	ND	ND	0.87	ND
4.	Absolute	ND	ND	ND	0.02
5.	Squeeze and Shine	0.31	ND	ND	ND
6.	Classic Nature	2.44	ND	1.56	ND
7.	Huad Colour	0.31	ND	0.56	0.31
8.	FBI	1.00	ND	0.62	0.30
9.	Midie	1.81	ND	0.19	0.19
10.	Juicy Lip Slimmer	0.62	ND	1.81	0.11

Table 2: Maximum Acceptable Concentration for Hg, As, Pb and Cd in (ppm) for cosmetic.

Locations	**As**	**Pb**	**Cd**	**Hg**
United State	0.0003	0.10	0.50	<1ppm
Germany	0.50	1.00	0.10	0.20
Canada	0.01	0.01	0.005	0.001

Source: Health Canada, (2012). Guardian on heavy metal impurity in cosmetics

Lip glosses are one of the most important sources of releasing heavy metals in the

environment and humans in particular as reported by Tracy (2013). Over exposure to these metals over time can lead to health problems such as neurological damage and increased cancer risk. Since heavy metals toxicity has exemplified the problem of environment pollution, it is necessary to know about the all possible sources. In this context, ten samples of lip gloss randomly collected at designated locations and were analyzed for the presence of mercury, arsenic, lead and cadmium as presented in table 1.

Arsenic: Arsenic was observed to be below detectable limit in 30% of the total samples analyzed for heavy metal. 30% of the total samples analyzed reveal that the concentrations of the metal were generally below the maximum acceptable limit for cosmetics (table 2). Generally, the study reveals that the metal show considerable higher concentration in 40% of the total samples tested for when compared to the Commission for Cosmetic Products at the federal Ministry of Health in Germany, the Guidelines for Canadian Drinking Water Quality and the United States Food and Drug Administration. The metal was detected in 70% (7 out the 10) samples in the range of 0.25ppm to 2.44ppm. The highest concentration of arsenic was observed in Classic nature with 2.44ppm. The second highest concentration of 1.81ppm was found in “Midie” product. Arsenic was not detected in the “Miss rose” product, “African Queen” product and The “Absolute” product, see table 1 and 2. High levels of Arsenic exposure can lead to health effects depending on route and the kind of arsenic exposed to as reported in the report on Human Biomonitoring of Environmental Chemicals in Canada: Results of the Canadian Health Measures Survey Cycle 1 (2007 – 2009). It was suggested by the ATSDR (2009) that the uptake of significant amounts of arsenic can intensify the chances of cancer development, especially the chances of development of skin cancer, lung cancer, liver cancer and lymphatic cancer. A very high exposure to arsenic can cause infertility and miscarriages with women, and it can cause skin disturbances, declined resistance to infections, heart disruptions and brain damage with both men and women. It was further reported that arsenic can damage DNA, nerve injury and stomachaches.

Lead: The results of lead concentration in the different lip gloss products are shown in table 1. Among the different samples analyzed, the highest concentration of lead was detected in “Juicy lip Slimmer product” with 1.81ppm followed by “Classic Nature” product with 1.56ppm while “Haud Colour” and “Midie” products showed lowest lead content of 0.56ppm and 0.19ppm respectively. Lead content was not detected in the “Absolute”, “Miss Rose” and “Squeeze and Shine” product. 40% of the samples analyzed reveal an increase in the concentration of the metal to be higher than the maximum acceptable limit for those of the Guidelines for Canadian Drinking Water Quality and the United States Food and Drug Administration but lower for the data obtained from the federal Ministry of Health in Germany. Generally, results from 30% of metal samples analyzed reveals that the metal concentration was higher than the maximum acceptable limit as outline in table 2 and 3. It was reported by the Campaign for Safe Cosmetics (2013) that lead is most damaging in children when they are six years and younger. Children are growing at a very fast rate - growing bones, developing stronger muscles and creating many connections in their brain. When lead instead of essential nutrients is "available" to the body to make bones, muscle, and brain connections, permanent harm to health can occur. Even at low levels, lead can be harmful and be associated with: Learning disabilities resulting in a decreased intelligence (decreased IQ), attention deficit disorder, behavior issues, nervous system damage, speech and language impairment, decreased muscle growth, decreased bone growth, Kidney damage, high levels of lead are life threatening and can cause seizures, unconsciousness, and death. They further stated that Lead exposure is a concern for adults, even though they have finished growing. Since an adult's body is much larger than a child's body, more lead is needed to cause injury but the harm lead can do to an adult is very serious. High levels of lead can cause: increased chance of illness during pregnancy, harm to a fetus, including brain damage or death, fertility problems in men and women, high blood

pressure, digestive issues, nerve disorder, memory and concentration problems, muscle and joint pain [U.S. Department of Health and Human Services (1993)].

Cadmium: cadmium was detected in 60% (six of the ten) lip gloss sample analyzed in this study. The highest concentration of cadmium was recorded in the "Huad Colour" samples with 0.31ppm, followed by the "FBI" samples with the concentration of 0.30ppm. The "Absolute" product recorded the least concentration of cadmium of 0.02ppm, followed by the "Miss Rose" product with 0.01ppm. Cadmium was not detected in "Black Opal, African Queen, Squeeze and Shine and Classic Nature" products. The concentration of Cd obtained for the analyzed samples reveals that the metal concentration was generally below the maximum acceptable limit as compared to those of the federal Ministry of Health in Germany, the Guidelines for Canadian Drinking Water Quality and the United States Food and Drug Administration (table 1 and 2). An exposure to significantly higher cadmium levels leads to a severely damage lungs and kidney, diarrhoea, stomach pains and severe vomiting, Bone fracture, Reproductive failure and possibly even infertility, Damage to the central nervous system, Damage to the immune system, Psychological disorders, Possibly DNA damage or cancer development [OSHA, (1998)].

Mercury: The result of this study reveals that mercury was not detected in the entire product tested. The use of products containing mercury can result in risk of illness or even death due to mercury poisoning. Mercury accumulates in the body, increasing the risk with each application. Additionally, family members can also be exposed, even if they aren't using the product. Mercury is added to cosmetic products such as body cream in an attempt to aid in skin lightening, anti – aging or blemish control. However, it seems unlikely that any effectiveness the product may have is worth the possible side effects of mercury poisoning, which include damage to the kidneys and nervous system, tremors, depression, memory problems, and even death [FDA Q & A, (2011)]. It can also interfere with the development of the brain in the unborn. Because mercury is sometimes listed under different names on the ingredient list (or imported products contain no ingredient list or the ingredient list is in a different language), it's likely that users of these products are unaware they contain mercury [Liu, *et. al.*, (2013)].

The total metals – Hg, As, Pb and Cd – detected was compared to the Maximum Acceptable Concentration of heavy metals for cosmetics as provided by Draft Guidance on Heavy Metal Impurities in Cosmetics (2010). The presence of these metals in the tested samples could be attributed to the fact that these metals occurs naturally in the environment and they can make their way in trace quantities into raw materials, and these substance in turn ends up as impurities in products that we consumes every day. Acceptable limits for heavy metals vary according to firstly, the subpopulation of interest (for example, children are more susceptible to heavy metal toxicity than adults and have greater exposure potential due to hand - to - mouth activity). Secondly, the amount of product used and thirdly, the site of application (for example arms versus lips) [Health Canada, (2012)]. The assessment of dermal absorption by a single component in a cosmetic product is complex and depends on factors such as the concentration in the product, the amount of product applied, the length of time left on the skin and the presence of emollients and/or penetration enhancers in the cosmetic product [Hostynek, (1998]. Thus, the metals analyzed in this study are not listed as ingredients on any of the products. Due to a lack of manufacturer testing and regulatory oversight, it is possible that the companies are not even aware that the products are contaminated with these toxic metals. These contaminants are likely to have gained entrance into the Lip gloss products when poor - quality ingredients are used. Most likely, these toxic metals could have been contaminants from one or more of the inorganic base materials used in the manufacturing processes [Health Canada, (2012)]. Since these toxic metals are found in various environments, manufacturers should test the raw ingredients for the presence of these toxic metals before their products are assembled into final products in order to track the origin of these contaminants.

Conclusion

Despite the concentrations of potentially toxic elements or metals, the overall potential exposure to the consumer is relatively high. But notwithstanding, heavy metals can build up in the body over time, the study notes, and are linked to a variety of health problems, "including cancer, reproductive and developmental disorders, neurological problems, memory loss, mood swings, nerve, joint and muscle disorders, cardiovascular, skeletal, blood, immune system, kidney and renal problems, headaches, vomiting, nausea and diarrhea, lung damage, contact dermatitis, brittle hair and hair loss. Matals are suspected hormone disrupters and respiratory toxins, and for some metals like lead, there is no known safe blood concentration level. So…what's in your makeup? How often do you use lip gloss on your children's lip? How often do you use lip gloss? Is your lip - gloss safe? Or is it harming you over the long - term? What are the manufacturers doing about it? What's their responsibility? Thus, it is feared however that the continuous use of lip gloss products contaminated with such heavy metals may however cause slow release of these metals into the human body and cause harmful effects to the consumers over time since these materials are easily ingested because they are worn on the lips. Extensive use of such products should be avoided until the situation is adequately addressed.

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