Determination Of Heavy Metal Levels In Lipsticks Samples Sold In Akilapa Market, Ibadan, Nigeria

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ABSTRACT

Heavy metals are known to be naturally occurring elements. They have high atomic weights and densities greater than that of water. They have wide applications and have been known to be generally toxic to plant and animal life even at low concentrations. Because of their high degree of toxicity, arsenic, chromium, cadmium, mercury and lead, are among the priority metals that are of public health significance. They are considered to be human carcinogens and are considered systemic toxicants which are known to induce multiple organ damage, even at lower levels of exposure. The brands of lipsticks investigated in this study were 50 which women commonly use in the city. The amount of lead, nickel, copper, cadmium, chromium, manganese, iron, zinc were investigated making use of Atomic Absorption Spectrophotometer (AAS) after the samples were properly digested. The results showed some of the heavy metals were found in various percentages, lead was found in 20% of the samples, cadmium (18%), chromium (8%), nickel (88%), iron (64%), manganese (24%), zinc(8%), and copper (24%). The concentration of chromium and zinc in all the samples is below 7ppm and 35ppm respectively, while the concentrations of other heavy metals such as manganese and iron are very high. This study confirm the presence of at least one heavy metal in all the lipstick samples analysed.

Keyword: Heavy metal, Lipstick, Carcinogens, Toxicity

INTRODUCTION

Lipstick is a cosmetic product containing pigments, oils, waxes, and emollients that apply colour, texture, and protection to the lips. Many colours and types of lipsticks exists. As with the other types of make-up, lipsticks are exclusively worn by women. Some lipsticks are also lip balms, they add colour and hydration (Oyedeji et al 2011). Some cosmetic products are used every day and are applied to the thinnest areas of facial skin, such as the pre-ocular areas and

lips, where absorption is very high, therefore the need for the products to be regulated for health and safety with concerns regarding the presence of harmful chemicals, including heavy metals in these products (Corazza *et al* 2009). Lipsticks usually contain heavy metals such as Lead, Nickel, Aluminium, Arsenic, Cadmium, Antimony and Chromium(Al-saleh and Al-enazi, 2011).

Virtually all metals can produce toxicity when ingested in sufficient quantities and there are some that can be very toxic even at very low concentrations (Oyedeji *et al* 2011). Metals such as lead, mercury, copper, manganese, cadmium, arsenic, nickel and zinc are usually referred to as heavy metals. Candace, 2016 reported that the first serious investigation of lead in lipsticks was in 2007 when the non-profit Campaign for safe Cosmetics tested a range of products and found traces of lead in 61% of named brand lipsticks. Lip products are presented in a wide variety of colours, which are produced by addition of pigments formulations (Valet, 2012).

Lead is one of the most toxic elements naturally occurring on earth. High concentration of lead can cause irreversible brain damage, seizure, coma and death if not treated immediately (Sanderson et al., 2006). According to Piccinini *et al*., 2013, heavy metal such as Lead (Pb) has been known to be an environmental contaminant that may occur in organic and inorganic forms, both naturally and from diverse anthropogenic activities. They reported that lead affects almost every system in the body, causing life-long adverse health effects. In their work, they observed that in some cases skin absorption of lead may remain undetected. In their conclusion, they opined that measures must be taken in limiting human exposure and controlling the amount of lead in consumer products. Pearce, 2007 reported that Lead has been known to be a highly poisonous metal which causes abdominal pain, headache, kidney failure, memory loss, weakness, male reproductive problems, pain and tingling in the extremities. Human skin absorption of soluble Lead acetate and Lead nitrate with increased levels in sweat, blood and urine within 6 h of skin application (Stauber et al., 1994).

Ozbek and Akman (2016) determined the amount of lead, cadmium and nickel in some hair dyes sold in Turkey. They found out that the concentrations of Pb, Cd and Ni in hair dyes were in the ranges of LOD-0.56 mg $g^{-}1$, LOD-0.011 ng $g^{-}1$ and 0.030e0.37 mg $g^{-}1$. Cadmium is one of the common known intoxicants to humans. Its presence in in nature and entrance to humans food chain causes serious damage in kidneys, lungs, bones and also anaemia and sometimes hypertension (Afshar et al.,2000). Naja and Volesky 2009 reported that accumulation of cadmium in the human body is a function of age and that cadmium in the renal cortex is

normally 5 – 20 times higher than that in the liver. They therefore concluded that chronic exposure to cadmium can result in lung disease, renal disease and fragile bones and that children should be protected from products such as nickel-cadmium batteries. Cadmium has been known to be an extremely toxic element and was classified as a human carcinogen according to WHO (Friberg and Elinder, 1992). However, when accidentally ingested and inhalaed, it becomes a much greater concern then dermal exposure (Department of Health and Human Services Public Health Service Agency for Toxic Substances and Disease Registry, 2012).

Nickel is reported to be one of the most common causes of allergic contact dermatitis. Nickel dermatitis produces erythema, eczema and lichenification of the hands and other areas of the skin that contact nickel. Exposure to nickel can also cause asthma, conjunctivitis and systemic reactions after parenteral administration of nickel – contaminated fluids and medication (Cempel and Nikel, 2006). Nickel is a carcinogenic metal. According to Chervona et al., 2012, Chronic exposure to Nickel has been connected with increased risk of cardiovascular disease, developmental deficits in childhood, neurological deficits, lung cancer, and high blood pressure. Also nickel is known to be an allergic substance which sensitizes the skin (Contado and Pagnoni, 2012). Nielsen et al. showed that repeated skin exposure to low nickel concentration has an effect on vesicle formation and blood flow (Nielsen et al., 1999)

Gerald 2018 reported that as important as iron (fe) is, its poisoning can be very fatal. It is a potential cause of fatal poisoning in children younger than age 5. He observed that within hours of iron poisoning, the chemical reaction of the cells begin to change and the liver begins to show signs of damage. Even though it is used in paediatric or prenatal vitamin and mineral supplement and for treatment of anaemia, iron overdose in adults is typically a suicide attempt (Clifford, 2018).

Chromium, though needed in human body to control glucose tolerance, fat levels in blood, reduction in arteriosclerosis, synthesis of proteins and resistance to infection, is considered lethal for a dose higher than 3g for adult human (Naja and Volesky, 2009). Overdose of chromium causes vomiting, diarrhoea, haemorrhagic diathesis and epitasis. While it was reported that repeated occupational inhalation of hexavalent chromium compounds can cause perforation of the nasal septum and skin ulceration.

Functions of copper in human body cannot be overemphasized. It functions in a number of important proteins and enzymes that are involved in iron and lipid metabolism, connective

tissue synthesis, maintenance of heart issues and central nervous system. It plays a role in cholesterol and glucose metabolism. It was reported to help in neutralising free radicals which can cause severe damage in cells (Scheiber, 2013). Though no toxicity has been reported from intake of about 3.5mg/day but doses greater than 10 -15 mg/day has been reported to cause vomiting (Afshar, 2000).Symptoms associated with the ingestion of fluids and foods contaminated with high quantities of copper usually include metallic taste and gastro intestinal distress, chronic and intermittent nausea, abdominal cramping and diarrhoea (Scheiber, 2013).

Zinc is an essential trace element and one of the several macronutrients that have recently received increasing attention because of their importance in maintaining the health and nutrition of the human population. However, excess of zinc in the body can be very harmful as it suppresses absorption of copper and iron (Muyssen, 2006). It was reported that excess free zinc can cause damage to the stomach lining through solubility of the zinc in the acidic stomach (Bothwell et al.,2003). Evidence shows that people taking 100 – 300mg of zinc daily may suffer induced copper deficiency and adversely affect cholesterol (Broadly et al., 2007).

Among the cosmetic products, lipsticks have the higher risks of direct oral ingestion, aggravating the negative effects of their ingredients. Therefore, people's concern about cosmetics toxicity has become an important issue. The worldwide use of lipsticks has been increasing due to the willingness of individual beautification (Soares and Talanta 2013).

The aim of this study was to determine the level of heavy metal poisoning in selected samples of lipsticks especially when they are built up in the body and to know whether or not they exceed the recommended level,

Description of Sampling Area

50 samples of lipsticks which were of different colours and makers were sampled at Akilapa market, Ogunpa, a popolar market in Ibadan, Oyo State, Nigeria. Details of manufacturers and number of samples from them is shown in Table 1

Sample Pre-treatment and Digestion method

Lipsticks are present in the semisolid form, therefore pre-treatment of samples are required before analysis. For this purpose, 1.0g of lipstick samples were exactly weighed with electrical analytical balance and put into digestion flask. They were then digested by using wet digestion method by repeatedly adding 5mL of $HNO_3/HClO_4$ in the ratio of 4:1, at interval of 5 minutes for 3 times on a hot plate at 100^oC in a fume cupboard. It was heated until white fumes started

evolving, which showed the completion of digestion process. The resulting digestate was filtered with filter paper and transferred to a 100.0mL capacity volumetric flask and made up to the mark by the addition of doubly distilled water and the concentration of the studied metal ions was then determined by flame atomic absorption spectrometry.

Sample Analysis

Lead, Cadmium, Chromium, Nickel, Copper, Manganese, iron and Zinc were determined by flame atomic absorption spectrometry using the recommended flame for each. Standard solutions were prepared in five different concentrations for each metal separately to obtain calibration curve for quantitative analysis. Deuterium lamp was used for background correction.

Table 1: List of manufacturers and the number of samples from each

S/N	Manufacturer's name	No of samples
1	Macc matte 24 hours lipsticks	8
2	Iman quality lipstick	7
3	Sleek make-up matte lipstick	13
4	Huadi lipstain	3
5	Milani 24 hrs matte lipsticks	5
6	Beyond beauty lipstick	1
7	Huda beauty matte lipstick	5
8	Miss lovely proof lipstick	4
9	Miss Corina lip gloss	2
10	Fully rose lip gloss	2

Instrumentation

The digested samples were analyzed for the concentration of lead, chromium, zinc, nickel, cadmium, iron, manganese and copper by atomic absorption spectrophotometer at conditions recommended by the manufacturers. The metals were determined at the most sensitive spectral lines of the metals. Appropriate hollow cathode lamp corresponding to the metal to be determined was used. The AAS was calibrated using calibration standards reagents for the metal to be analyzed. The calibration curves were prepared separately for all metals by running different concentrations of standard solutions. The instrumental responses for the calibration working standard were used to plot the calibration curves for the metals automatically by the

instrument and the concentration was extrapolated from the calibration graph. Each sample was then aspirated, and the results were recorded. Operational condition for the metal analysis is given in Table 2.

Preparation of blank

A blank was prepared to account for possible contribution from acid or distilled water. 5mL of a mixture of concentrated Nitric acid and perchloric acid was measured and transferred into the digestion flask containing some mL of the distilled water, it was then digested and transferred into a 25mL standard flask and made up to the mark with distilled water.

Table 2: Operational condition for the metal analysis

Metal	Wavelength(nm)	Relative sensitivity	Detection limit
Pb	217.0	1.0	0.05
Cd	228.9	1.0	0.002
Cr	357.9	1.0	0.002
Ni	341.5	1.0	0.001
Zn	213.9	1.0	
Mn	279.5	1.0	0.7
Fe	248.3	1.0	0.01
Cu	324.7	1.0	0.002

Results and Discussion

The results of heavy metals determined in this study are presented in Tables 3 and 4. Lead was found in only ten out of the fifty samples (20%) with a mean value of 28.50 ppm, and with only six samples above the FDA limits (i.e, 20 ppm). Lead was not found in the huadi lip stain, beyond lipstick, huda beauty lipsticks, fully roses lipsticks,miss corina lipstick and miss lovely proof lipstick. The lipsticks in which lead are found are the Macc matte 24 hrs lipstick, Iman quality lipstick, Sleek make-up matte lipstick and the Milani 24hrs matte lipsticks, with the range from (1-106) ppm(Fig 1). Al- Saleh and Al-Enazi (2011) reported that the use of metals as ingredients in cosmetics is prohibited in many advanced countries, but metallic impurities cannot be totally avoided even under good manufacturing processes, because they exist naturally in the environment. The level can only be minimized. There is a wide range of lead gotten from this research work as compared to that obtained by Roopa and Mallikarkun, 2017,

who reported that the ranges of Lead in the lipsticks analyzed is 0.4 – 21.80 ppm. The higher range might be due to environment/ Industrial impurities and contaminations.

Table 3: Results of heavy metals in each lipstick samples (N.B: All readings are in ppm)

Lipstick S/N	Pb	Cd	Cr	Ni	Fe	Mn	Zn	Cu
LP 01	36.00	68.50	ND	ND	494.85	ND	3.00	22.00
LP 02	41.00	44.00	1.00	16.00	ND	6.50	ND	ND
LP 03	41.00	56.20	ND	ND	35.85	ND	14.00	14.00
LP 04	106.00	11.70	3.60	ND	66.85	ND	27.00	8.00
LP 05	1.00	ND	ND	10.00	35.85	14.50	ND	110.40
LP 06	ND	ND	ND	7.00	ND	19.50	ND	ND
LP 07	ND	ND	ND	9.00	ND	16.5	ND	ND
LP 08	20.00	9.40	6.80	ND	646.85	ND	34.00	26.00
LP 09	ND	ND	ND	7.00	12.85	3.50	ND	102.30
LP 10	ND	ND	ND	8.00	ND	18.50	ND	ND
LP 11	ND	ND	ND	9.00	26.85	6.50	ND	117.10
LP 12	ND	ND	ND	8.00	0.85	35.50	ND	ND
LP 13	ND	ND	ND	8.00	31.85	39.50	ND	ND
LP 14	29.00	ND	ND	9.00	ND	175.50	ND	ND
LP 15	ND	ND	ND	7.00	ND	8.50	ND	ND
LP 16	ND	ND	ND	9.00	ND	9.50	ND	ND
LP 17	ND	ND	ND	5.00	ND	11.50	ND	ND
LP 18	ND	ND	ND	9.00	29.85	75.50	ND	ND
LP 19	ND	ND	ND	8.00	ND	14.50	ND	ND
LP 20	ND	ND	ND	12.00	10.85	12.50	ND	111.40
LP 21	ND	ND	ND	12.00	ND	9.50	ND	ND
LP 22	ND	ND	ND	20.00	30.85	73.50	ND	ND
LP 23	ND	ND	ND	10.00	ND	9.50	ND	ND
LP 24	ND	ND	ND	6.00	43.85	113.50	ND	ND
LP 25	2.00	ND	ND	5.00	ND	4.50	ND	ND
LP 26	ND	ND	ND	2.00	ND	73.50	ND	ND
LP 27	ND	ND	ND	6.00	ND	118.50	ND	ND

LP 28	ND	ND	ND	3.00	ND	133.50	ND	ND
LP 29	1.00	2.00	ND	6.00	6.85	42.50	ND	61.30
LP 30	ND	2.00	ND	6.00	ND	3.50	ND	ND
LP 31	8.00	ND	ND	4.00	ND	11.50	ND	ND
LP 32	ND	ND	ND	7.00	27.85	66.50	ND	ND
LP 33	ND	ND	ND	7.00	ND	13.50	ND	ND
LP 34	ND	ND	ND	10.00	17.85	214.50	ND	ND
LP 35	ND	181.00	4.70	7.00	16.85	43.50	ND	ND
LP 36	ND	3.00	ND	1.00	ND	62.50	ND	ND
LP 37	ND	ND	ND	1.00	ND	ND	ND	ND
LP 38	ND	ND	ND	5.00	ND	ND	ND	ND
LP 39	ND	ND	ND	1.00	ND	55.50	ND	ND
LP 40	ND	ND	ND	3.00	ND	ND	ND	ND
LP 41	ND	ND	ND	6.00	ND	ND	ND	47.90
LP 42	ND	ND	ND	7.00	ND	ND	ND	48.70
LP 43	ND	ND	ND	1.00	ND	ND	ND	ND
LP 44	ND	ND	ND	2.00	192.50	ND	ND	ND
LP 45	ND	ND	ND	ND	ND	35.50	ND	ND
LP 46	ND	ND	ND	1.00	ND	ND	ND	ND
LP 47	ND	ND	ND	ND	ND	58.50	ND	ND
LP 48	ND	ND	ND	4.00	ND	79.50	ND	ND
LP 49	ND	ND	ND	5.00	24.85	ND	ND	ND
LP 50	ND	ND	ND	1.00	ND	68.5	ND	ND
Blank	5.00	4.00	ND	ND	14.15	0.50	ND	12.00

Table 4: Lowest, Highest and mean values of heavy metals in Lipsticks

Heavy metals	Lowest value in all (ppm)	Highest in value all (ppm)	Mean value ± Standard deviation
Pb	1.00	106.00	28.50±31.767
Cd	2.00	181.00	41.98±58.020
Cr	1.00	6.80	4.03±2.414
Ni	1.00	20.00	6.59±3.979
Fe	0.85	646.85	86.79±178.648
Mn	3.50	214.50	51.37±54.762

Zn	3.00	34.00	19.5±13.772
Cu	8.00	117.90	60.83±42.33

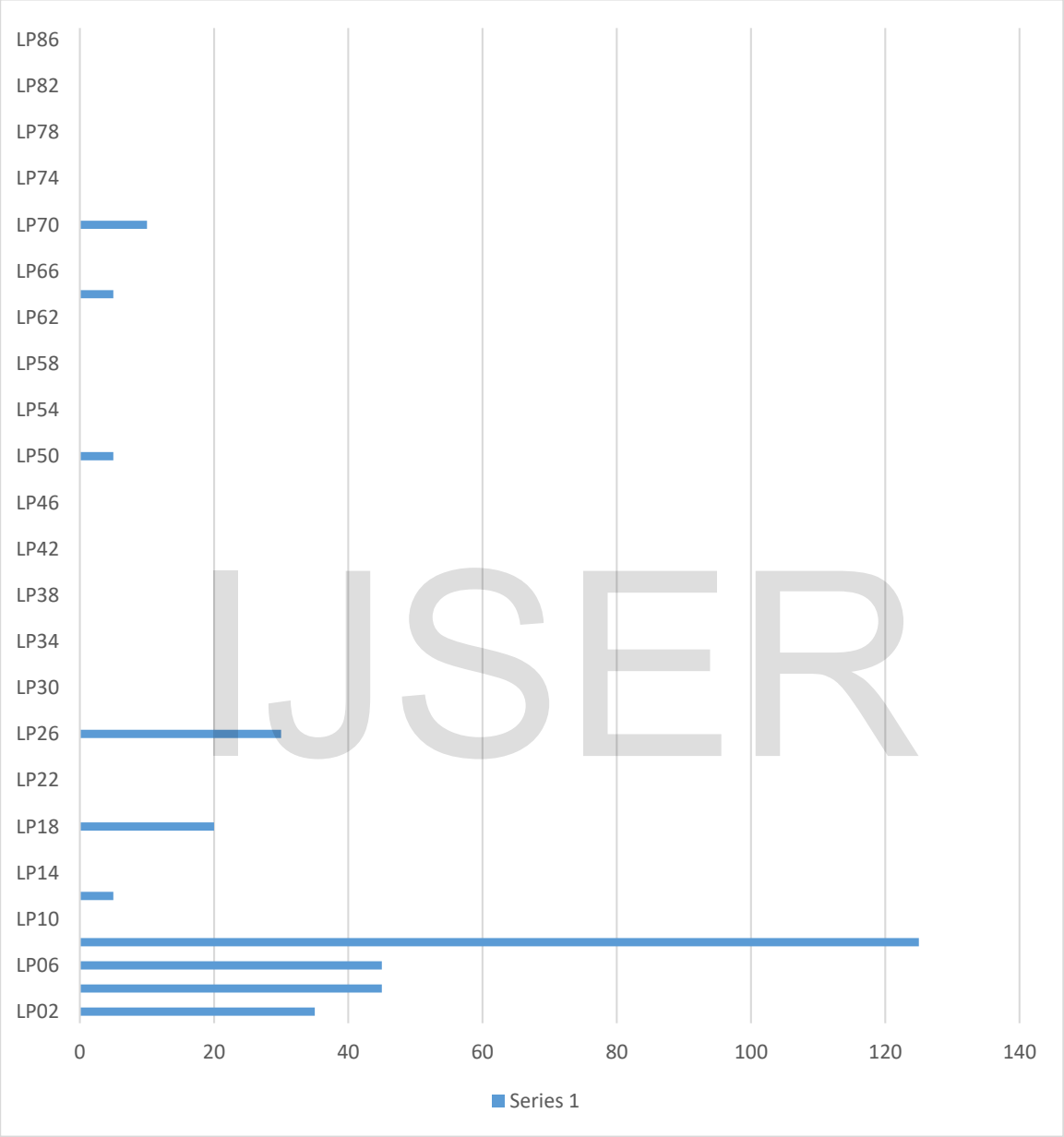

Figure 1: Bar chat of levels of Lead in the lipsticks samples

Cadmium was found in nine out of the fifty samples (18%) with a mean value of 41.98ppm. Six of the samples were above the FDA limits (5ppm). The highest level of Cadmium was in the Huda beauty matte lipstick as shown in Fig.2. Afshar *et al*., 2000 reported that entrance of Cadmium to human's food chain causes serious damage in kidneys, lungs, bones and also

anemia. Therefore, monitoring its level in lipstick samples is very important to avoid accumulation in the human system.

Chromium was found in four of the fifty samples (8%) with a mean value of 4.03ppm. The highest level was in Macc matte 24 hours lipstick. This result is in agreement with Khalid *et al*., 2013 who reported a range of 0.222 – 5.430ppm. Though Chromium is not

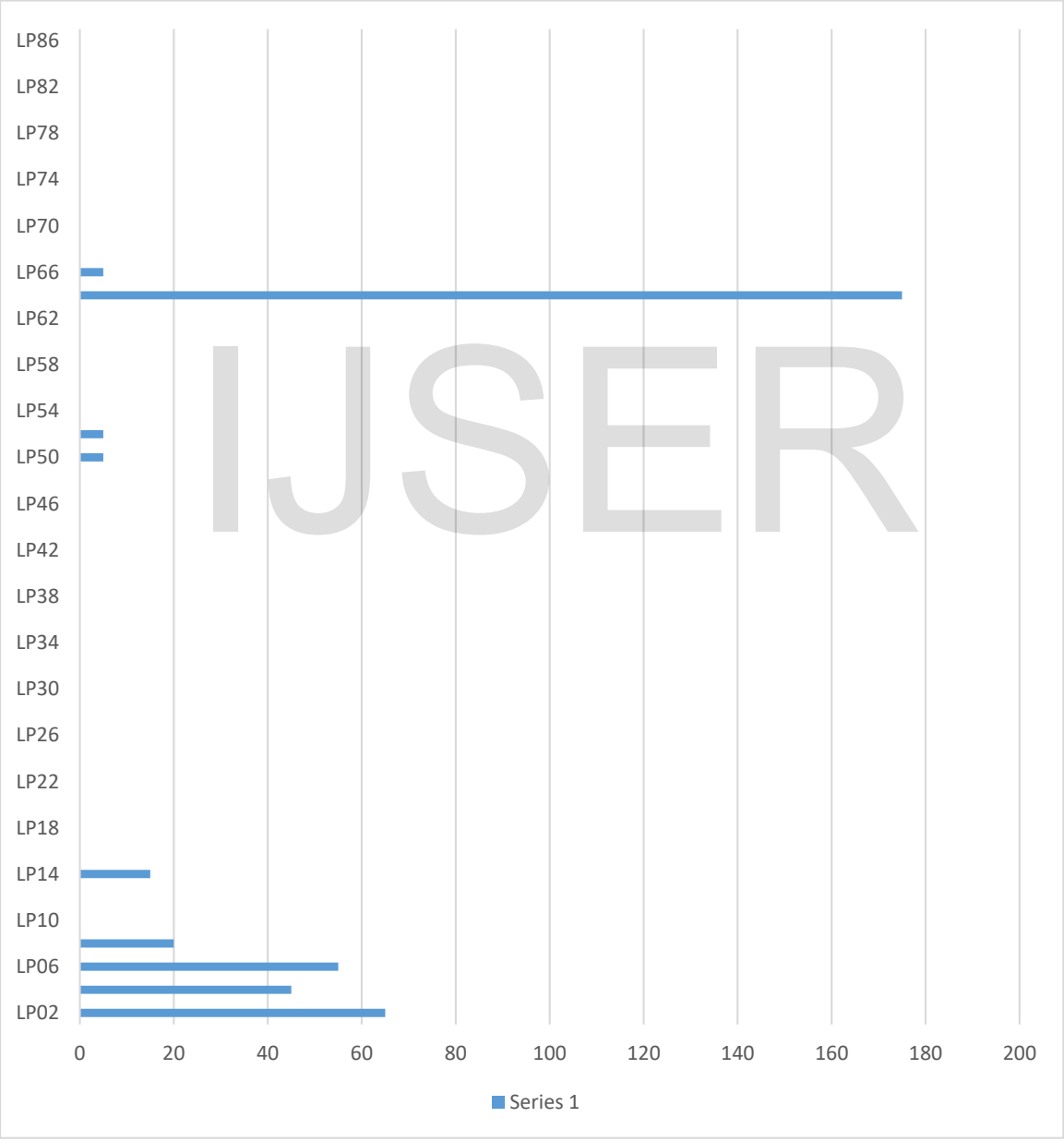

Figure 2: Bar chat showing the level of Cadmium in the lipsticks samples

directly an ingredient in lipstick but the source could be traced to impure raw materials and inadequate monitoring of production system. Although no reports indicate that Chromium salts have severe toxic effects (Naja and Volesky, 2009) but toxicity may occur at very high level.

Nickel was found in the majority of the lipsticks samples (88%) and only six (6) out of the fifty samples do not contain nickel as an impurity, therefore there is need for proper investigation and monitoring of the presence of nickel in lipsticks (Fig.3).

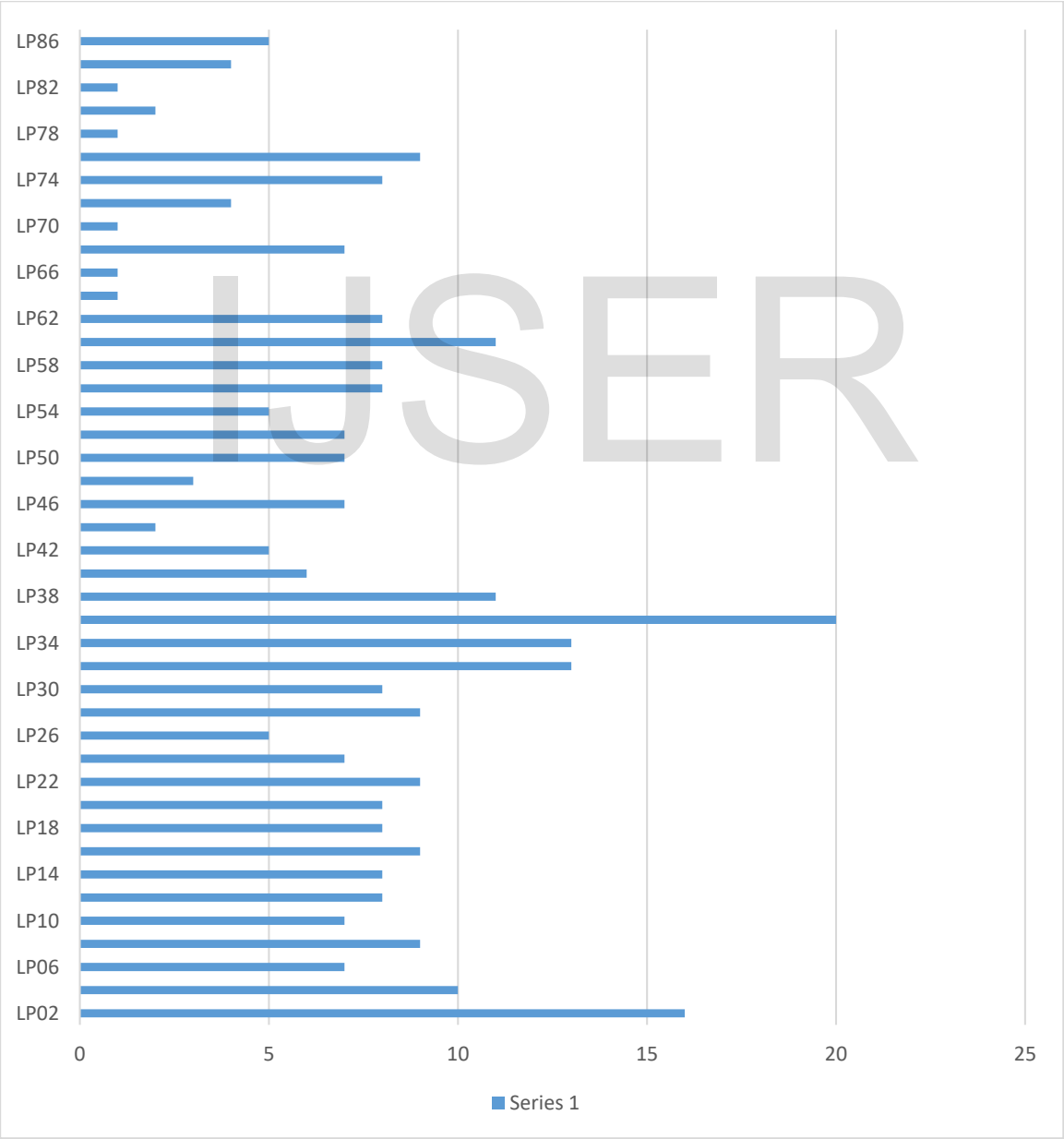

Figure 3: Bar chat showing level of Nickel in the lipsticks samples

It was found to be in the range (1-20) ppm with a mean value of 6.59ppm as shown in Table 3. The maximum acceptable limit of nickel in cosmetics is 0.6 ppm , therefore, the nickel detected in all the lipsticks is higher than acceptable limits. Khalid et al., 2013 also reported the presence of nickel in lipsticks at levels higher than acceptable limits ranging from 0.6-5.947 ppm.

The presence of iron (Fe) was detected in eighteen of the fifty samples (36 %). The values obtained ranged from 0.85-646.83 ppm with a mean of 86.79 ppm. Though iron is one of the trace elements needed by the human body but the level still need to be monitored to prevent adverse effect.Manganese was present in twelve samples with the level ranging from 3.50-214.50 ppm and the mean of 51.37 ppm. Ali *et al* ., 2016 reported the presence of manganese in lipsticks with the range 2.45-22.06 ppm. Though there is wide variation in the results we obtained, this may be due to our higher sampling number. Manganese has been regarded as one of the toxic heavy metals but it is essentially in very small quantity.

Zinc was present in four samples with levels in the range 3.0-34.0 ppm and a mean of 19.5 ppm (Fig.4). Though Zinc is an essential element required for good health, its excess can be harmful in the body by suppressing the presence of other essential metals (Carlous 2010). The presence of copper was observed in eleven samples which implies 22%. It was noted that four of the samples that contain lead also contain copper. The copper values in the lipstick ranges from 8.0-117.9 ppm.

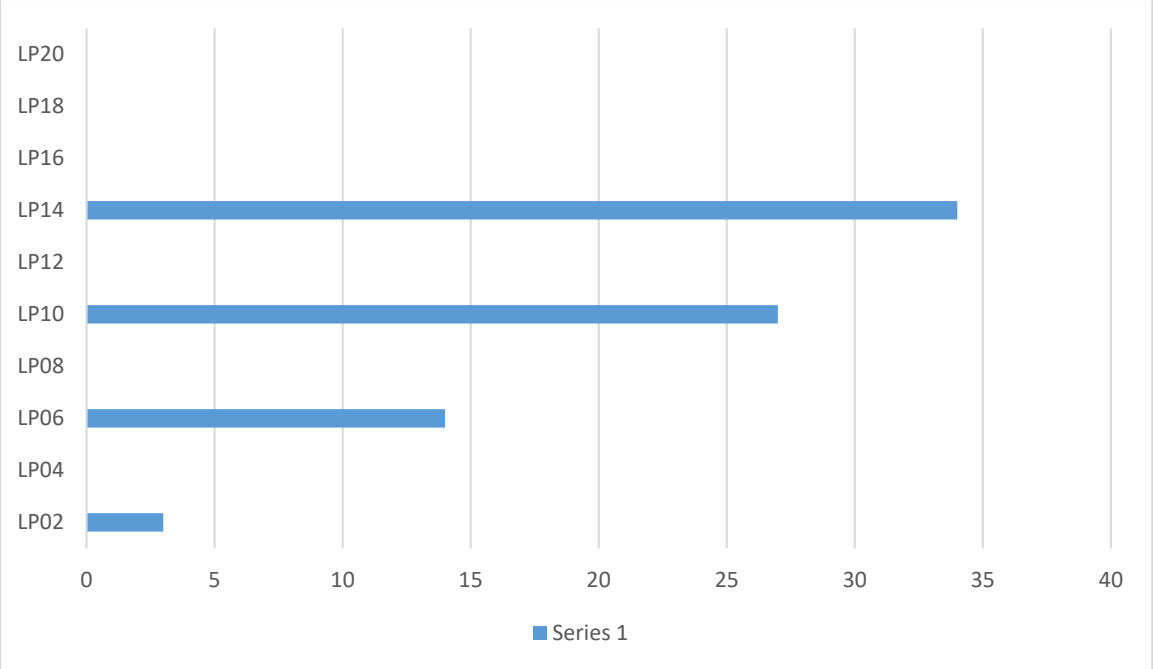

Figure 4: Bar chat showing the level of Zinc in the lipstick samples

Conclusion

The data presented in this work provides useful information about heavy metals content in Nigerian cosmetic lip products. It was observed that apart from Chromium, values obtained for other metals are well above the acceptable limits. It is hereby recommended that appropriate Government agency saddled with the responsibility of monitoring the manufacturing processes of these products live up to expectation so as to prevent accumulation in users' blood hence protecting public health.

DISCLAIMER

The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

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