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Determination of Cadmium, Lead, Nickel and Zinc in Hair Cream Products on the Nigerian Market

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Abstract
In this study, heavy metals like Pb, Cd, Ni and Zn were quantitatively estimated using AAS. The results indicate that among the toxic heavy metals, Pb, Ni and Pb were exceeding the Health Canada permissible limit fixed for hair creams in most of the hair cream samples, but Cadmium was found appreciably well below the permissible limit. At 95% confidence level, $p < 0.05$, there is a significant difference in the values of the concentration of heavy metals among the hair cream samples used in this study, except for Cadmium concentrations which at this confidence level, $p > 0.05$, has no significant difference. In conclusion, enforcement of strict and separate regulatory guidelines and promotion of Good Analytical Practice (GAP) and Good Manufacturing Practices (GMP) is suggested for hair cream cosmetics by Health Canada and other regulatory agencies in Nigeria. This study presents the status of heavy metals in marketed hair cream cosmetic formulations and also provides a simple and convenient AAS method which can effectively be adopted at Industrial level for the quality control and standardization of hair care cosmetic preparations and other related products.
Keywords: Hair cream cosmetic, Heavy metals, AAS, GAP, GMP

1. INTRODUCTION

A cosmetic product is any substance or preparation intended to be placed in contact with the various parts of the human body (epidermis, hair system, nails, lips and external genital organs) or with the teeth and the mucous membranes of the oral cavity with a view exclusively or mainly to cleaning them, perfuming them, changing their appearance and/or correcting body odors and/or protecting them or keeping them in good condition [1]. They are articles intended to be rubbed, poured, sprinkled, or sprayed on, introduced into, or otherwise applied to the human body or any part thereof for cleansing, beautifying, promoting attractiveness, or altering the appearance [2]. This definition includes a myriad of products used by men and women: hair creams, skin-care creams, lotions, powders and sprays, perfumes, lipsticks, fingernail polishes, eye and facial makeup, permanent waves, hair colors, deodorants, baby products, bath oils, bubble baths, and mouthwashes.

Although cosmetics prior to the 1960s had a good safety record, there are examples when this was not the case. For example, from the classical times through the middle ages up to the early 20th century, make-up dyes contained highly toxic heavy metals, such as Lead, Mercury and Cadmium oxides. In the 1930s, thallium-containing depilatory products caused cases of severe and occasionally lethal intoxications [3]. During 1958/1959 halogenated salicylanilide-containing cosmetics produced an epidemic of photo-allergic reactions in the UK and elsewhere [4], and, in the 1950/60s, Zirconium-containing deodorants and hair creams resulted in an outbreak of long-lasting allergic inflammatory skin and hair scalp reactions in consumers in Europe and the US [5].

Lead poisoning has been a recognized health hazard for more than 2,000 years. Characteristic features of Lead toxicity, including anemia, colic, neuropathy, nephropathy, sterility and coma. Exposure to low-levels of lead has also been associated with behavioral abnormalities, learning impairment, decreased hearing, and impaired cognitive functions in humans and in experimental animals [6]. There have been a number of reports in the media and on internet about the presence of lead in branded cosmetic products [7]. Studies have revealed that many kohl eyeliners containing serious levels of lead are imported from India, Arabia and the Middle East. Long exposure to lead can bring on hypertension, caused through kidney damage. Some studies from [7] have revealed that lead from kohl can enter the body through skin absorption in children's as well as in their parents.

Cadmium is a deep yellow to orange pigment and mostly present in lipsticks and face powders. The use of cadmium in cosmetics products are due to its color property as it has been used as a color pigment in many industries [8]. Metals are well-recognized causes of allergic contact dermatitis (ACD) both at occupational and environmental level. Various research aimed at exploring occupational, clinical, toxicological and environmental exposure of trace metals along with their impact on human health [9, 10, 11, 12, 13, 14] have been carried out. The key metals involved in this pathology are, in order of incidence, Ni, Co, and Cr, either taken alone or in their association [15, 16, 17].

Basically, Ni is considered the primary source of causing ACD with a prevalence of 20% in females and 1% in males [18]. This is mainly due to the free Ni ions released from objects containing Ni – which daily came in contact with the skin (i.e., piercing, jewels, buttons, clasps, coins, etc.) – corroded by the human sweat. In order to reduce the Ni ACD, the release of this metal from various objects has been regulated by the European Council Directive communities (1994). Although many studies have been reported the presence of above metals in cosmetic products especially in lipsticks and nail polish, however data about their presence in hair creams is scanty. Present study thus planned to see if hair cream cosmetics manufactured here in Nigeria are contaminated with Cadmium, Lead, Nickel and Zinc.

2. MATERIALS & METHODS

2.1 Sample collection

Ten majorly marketed hair creams labeled (PX, AT, COC, DM, FEM, APP, SW, SM, S-8 and TS) were used for this study, and for each of these ten hair creams selected, three batches comprising of three samples & making a total of thirty samples for this study were collected for this study. The samples were bought from major markets (Sabon-Gari central market, Samaru general market, Tudun wada and Zaria city markets) in Zaria metropolis, Kaduna state in Nigeria. The country of manufacture was ascertained as all the hair creams contained the serial number for the registration of the cosmetic product by National Agency for Food and Drug administration and Control (NAFDAC) in Nigeria. The Container label information on collected hair cream samples is given in Table-1 below with figure 1 showing the sampling area.

Figure-1: Map showing the sampling area

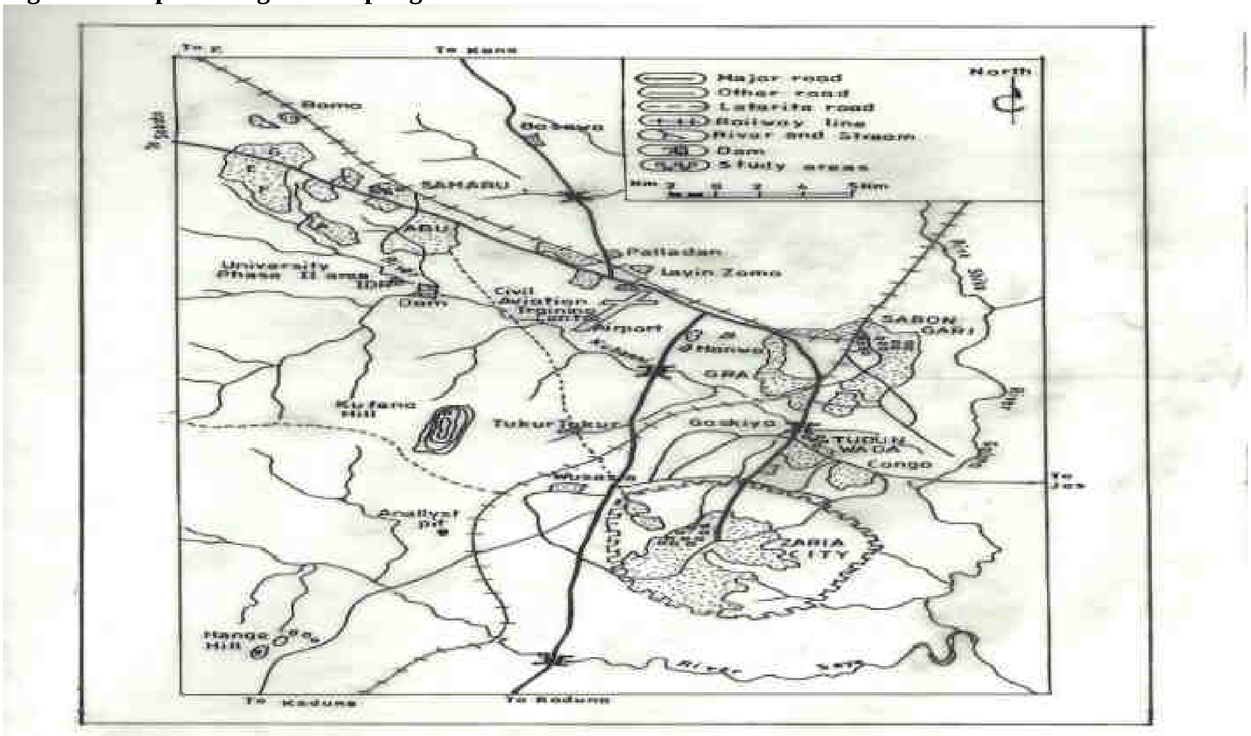

Table 1: Container label information on collected hair cream samples

Product Code	Manufacture date	Expiry date	NAFDAC No.	Batch No.
PX	+	+	+	+
AT	-	-	+	-
COC	-	-	+	-
DAM	+	+	+	+
FEM	+	+	+	+
APP	+	+	+	+
SW	-	-	+	-
SM	+	+	+	+
S8	-	-	+	-
TS	-	-	+	-

(+) Label disclosure provided, **(-)** Label disclosure not provided

PX: Promax, **AT:** Angel Touch, **COC:** Coconut oil, **FEM:** Femoon, **APP:** Apple, **SW:** Sports waves, **SM:** Soul mate, **S8:** Sulphur-8, **TS:** Top sheen

2.2 Sample Preparation

Sample preparation for heavy metal analysis was done under standard procedure. Briefly, a representative 3g sample was mixed with 0.5g of finely ground potassium permanganate and then 1.0ml of concentrated sulfuric acid was added while stirring. A strong exothermic reaction occurred. The sample was then treated with 2ml concentrated nitric acid. 10ml of concentrated HCl was then added and the sample was heated until the reaction was complete and is then filtered. The filter was washed with hot concentrated HCl. The filter paper was transferred to a digestion flask, treated with 5ml of concentrated HCl. The sample was brought to volume and analyzed by AAS.

Chemicals of analytical grade purity and distilled water were used in the preparation of reagents. All glassware used were washed and rinsed with distilled water before drying in the oven. The reagents required were purchased from Stevemoore Chemicals, Emanto, Zaria, Kaduna State, Nigeria. All the experiments were performed in triplicate and the average values were reported. Statistical analysis was carried out using SPSS to describe the pattern of distribution of the heavy metals in all the samples under study & ANOVA was used to compare test parameters using the SPSS 16 software. Four metals i.e. Cadmium, Lead, Nickel and Zinc were analyzed through Atomic Absorption Spectrophotometer (Varian AA240FS sequential Atomic Absorption Spectrometer).

2.3 Preparation of Stock Solution of stock solution

2.3.1 Cadmium solution: 2.01g of Cadmium sulphate, $CuSO_4.H_2O$ was dissolved in distilled water and made up to 1L.

2.3.2 Lead Solution: 1.5985g of Lead (II) trioxonitrate (V) $Pb(NO_3)_2$ was dissolved in distilled water and made up to 1L.

2.3.3 Zinc solution: 1.2449g of Zinc (II) oxide, ZnO was dissolved in 5cm^3 distilled water and 25moldm^3 HCl and the solution made up to 1L with dissolved.

2.3.4 Nickel solution: 7.0365g of Ammonium Nickel Sulphate hexahydrate, $NiSO_4$. $(NH_4)_2SO_4.6H_2O$

The method of standard addition which is considered as a validation method was used to demonstrate the validity of our method. Hence, a recovery test was performed using method of standard addition. Standard solutions containing Cd, Pb, Ni and Zn were prepared and spiked with digested samples, after dilution of sample to 50 ml [19].

2.3.5 Preparation of Calibration Curve

Appropriate working standards for each metal were prepared by serial dilution of stock solution. The working standards solutions were aspirated into the flame and their absorbance recorded. A calibration curve was prepared by plotting absorbance against concentration.

2.3.6 Analysis of Sample

The digested sample solution was aspirated into the flame and the absorbance values recorded. The metal concentration was calculated from the calibration curve. The instrumental conditions used are given in Table-2 below

Table-2
Instrumental conditions for AAS determination of metals with Varian AA240FS sequential Atomic Absorption Spectrometer

Element	Wavelength (nm)	Band pass (nm)	Flame type	Fuel flow rate L/Min
Cd	228.8	0.5	Air/C_2H_2	1.2
Pb	217.0	0.5	Air/C_2H_2	1.1
Zn	213.9	0.5	Air/C_2H_2	1.1
Ni	341.5	0.5	Air/C_2H_2	1.1

2.3.7 Statistical Analysis
Statistical analysis was carried out using SPSS to describe the pattern of distribution of the heavy metals in all the samples that was under study, while ANOVA and Pearson Correlation analysis was used to compare test parameters using the SPSS 16 software [20].

2.3.8 Validation of Experimental Protocol (Spiking Experiment)
Preparation of Multi-element standard solution (MESS), 0.3055 g Ni $(SO_4)_2.6H_2O$ was weighed out and dissolved in 2 ml distilled water in a beaker and transferred into a 500 ml volumetric flask. The beaker was then rinsed thoroughly with distilled water into the flask. 0.1298g Zn (NO3)2 was also weighed out and dissolved in distilled water and HNO_3 respectively and then transferred into the same volumetric flask. 0.0799 g $Pb(NO_3)_2$ was weighed and dissolved in 2 ml HNO3 in a beaker, distilled water was added and then transferred into the same volumetric flask. Lastly, 0.13442 g of Cd $(NO_3)_2$ was weighed out and dissolved in 2 ml distilled water in a beaker and transferred into same 500 ml volumetric flask and the beaker was rinsed thoroughly with distilled water into the flask. The flask was then made to mark with distilled water to give the Multi-element standard solution (MESS). Aliquots of this solution were used in the spiking experiment. The hair cream was digested in triplicates together with the blanks and run on the AAS machine. The amount of metal present in the sample was determined from the calibration Curve. These gave the amount of metal in the unspiked sample and provide the basis for spiking experiment.

5 ml of the Multi element standard solution was drawn with graduated pipette and used to spike 3g of the hair cream sample. These were then digested in triplicates together with their blanks and then run on AAS. Concentrations of the metals in spiked and unspiked samples were used to calculate the percentage recovery in order to validate the method

3. RESULT AND DISCUSSION
The heavy metals levels are given in Table-3. All the hair cream products in this study were found to contain substantial levels of Lead (Pb), Nickel (Ni), Cadmium (Cd) and Zinc (Zn).

3.1 Lead (Pb) Level
Lead (Pb) ranged from 44.22 – 013 mg/kg as shown in Table-3, SM having the highest mean value of 44.22 ± 0.036 mg/kg and COC having the lowest value of 0.13 ± 0.012 mg/kg with SM, S-8, AT, PX, APP and FEM having Lead (Pb) values of 44.22 ± 0.036 mg/kg, 41.59 ± 0.083 mg/kg, 40.67 ± 0.075 mg/kg, 39.35 ± 0.007 mg/kg, 37.60 ± 0.029 mg/kg and 34.25 ± respectively. These values are very high compared to the results reported by [21,22]. They are also higher than the maximum permissible limit of 10mg/kg as stipulated Canadian health, TS DAM and COC with values 0.90 ± 0.032 mg/kg, 0.33 ± 0.004 mg/kg and 0.13 ± 0.012 mg/g respectively, fell below the maximum permissible limit. The trend in the Lead concentration in mg/kg is given as SM>S8>AT>PX>APP>FEM>SW>TS>DM>COC. Lead (Pb) is one of the most popular heavy metals in elemental analysis, possibly due to the numerous adverse health challenges it creates in various organs of the human body. The presence of high Lead (Pb) might be due to the use of utility water obtained from Lead pipes used in the preparation of hair cream formulations. Lead acetate is not left out also as it has been found useful as color additives used in hair cream formulations. ANOVA summary table shown in Table-4 shows that at 95% confidence value, $p<0.05$, implying that there is a significant difference among the Lead (Pb) values of all the hair creams under study.

3.2 Cadmium (Cd) Level
The Cadmium level ranged from 0.440 – 0.00 mg/kg as shown in Table-3 with DAM having the highest mean value of 0.440 ± 0.381 mg/kg, while APP and PX are non- detectable. The trend in the Cadmium concentration in mg/kg is given as DM>TS>SW>SM>COC>S8>AT>FEM. The Cadmium content of the hair creams investigated were very low compared with the results reported by [21, 22]. It is also observed to be the maximum permissible limit of 3 mg/kg stipulated by Health Canada, 2012. Cadmium might have being used as coloring pigment in the hair creams under study. Although the presence of Cadmium in the samples were in trace amount but the slow release of Cadmium with low amount may also cause harmful effects to the human body. The presence of Cadmium has also been reported in various lipsticks [8]. It does not have to be present in

abundance in products to produce hypertension. In fact, results from tests showed that it was minor exposure that caused high blood pressure. When Cadmium was injected directly into the subject it caused blood pressure to rise. So the small amounts are not safe. It targets blood vessel and heart tissue, as well as, the kidneys, lungs and brain, and results in heart disease, hypertension, liver damage, suppressed immune system and other nasty symptoms [8]. ANOVA Summary table shown in Table-4 shows that at 95% confidence value, $p>0.05$, implying that there is no significant difference among the Cadmium values of all the hair creams under study.

3.3 Nickel (Ni) Level

The Nickel level ranged from 173.03 – 7.03 mg/kg as shown Table-3 with FEM having the highest mean value of 173 ± 0.005 mg/kg and SM having the lowest value of 7.03 ± 0.003. The trend in the Nickel concentration in mg/kg is given as FEM>PX>AT> DAM>S8>COC>SW>TS>APP>SM. The Nickel content of the hair creams investigated were very high compared with the results reported by [23] on levels of Nickel and other potential allergenic metals in Ni- tested commercial body creams and higher than the maximum permissible limit of 3 mg/kg by Health Canada, 2012. It has been stated that Ni actually represents the main cause of contact dermatitis; minimal amounts of other toxic metals can also trigger a pre-existing allergy. Nickel dermatitis produces erythema, eczema and lichenification of the hands and other areas of the skin that contact nickel. Initial sensitisation to Nickel is believed to result from dermal contact but recurring flares of eczema, particularly of the hands, may be triggered by ingestion. Reactions to Ni were not isolated but associated with Cr, Co, and Pd sensitivity [24, 25, 26]. This study also revealed that the maximum content (173.03 ± 0.005) mg/kg of Nickel in the hair cream products under study is higher than those obtained by [27] for eyeliners (9.2 ± 4.10) mg/kg, eye pencils (13.4 ± 5.80) mg/kg and lipsticks (14.6 ± 6.30) mg/kg. Basically, Ni is considered the primary source of causing Allergic Contact Dermatitis (ACD) with a prevalence of 20% in females and 1% in males [28]. This is mainly due to the free Ni ions released from equipment containing Ni – which might have been used in the preparation of the hair cream formulations. Nickel is a silver-white metal generally used to enhance the value, utility, and lifespan of industrial equipment and components by protecting them from corrosion. Nickel is also commonly used in the chemical and food processing industries to prevent iron contamination. The high level of Nickel may also be attributed to the fact that it may have been used to protect most of the industrial equipment used in the production of the hair creams from corrosion. ANOVA summary table shown in Table-4 below shows that at 95% confidence value, $p<0.05$, implying that there is a significant difference among the Nickel (Ni) values of all the hair creams under study.

3.4 Zinc (Zn) Level

The Zinc level ranged from 14.47 – 2.19 mg/kg as shown in Table-3 with TS having the highest mean value of 14.47 ± 0.060 mg/kg and DAM having the lowest value of 2.19 ± 0.011 mg/kg. The Zinc content of the hair creams investigated are generally low compared with the results reported by [22]. TS (14.47 ± 0.060 mg/kg), PX (7.56 ± 0.350 mg/kg), COC (4.60 ± 0.050 mg/kg), SM (14.47 ± 0.060 mg/kg), S-8 (5.69 ± 0.08 mg/kg), FEM (6.81 ± 0.028 mg/kg), AT (3.48 ± 0.028 mg/kg) and SW (3.11 ± 0.026 mg/kg) have values greater than the 3 mg/kg stipulated by Health Canada, 2012. The trend in the Zinc concentration in mg/kg is given as TS>PX>FEM>S8>SM>COC>AT>SW>APP>DAM. The presence of Zinc in these sample can be attributed to the fact that, Zinc sulphate has been known to be used in hair care cosmetics as an astringent, biocide and an antimicrobial agent and could have being added as part of the constituents of these hair creams and wasn't mentioned as an ingredients in the ingredient list. ANOVA summary table shown in Table-4 below shows that at 95% confidence value, $p<0.05$, implying that there is a significant difference among the Zinc values of all the hair creams under study. The presence of these heavy metals in the hair cream cosmetics may make it toxic to the scalp; the incorporation of elements into the keratin structure of hair takes place by binding to the sulfhydryl groups that are present in the follicular protein. In this regard, it should not be overlooked that detergents such as soap and shampoos, hair creams, lotions, hair bleaches and dyes actually compete with the complexing ability of these reactive sites, thus leading to a significant leaching of elements from the shaft bulk into the body system [29]. Apart from the fact that they cause blood poison, they also destabilize formulation system of the hair cream by forming free-radicals thereby reducing their shelf-life. Therefore efforts should be made to make sure that these metals are absent in hair care cosmetics as much as possible. This can be achieved by complexing with chelating compounds like EDTA [30]. The World Health Organization is silent regarding the maximum permissible limits of heavy metals in hair care cosmetics. In this case, Health Canada has taken the initiative and implemented a few measures to control heavy metal concentration in cosmetics and gave the maximum acceptable limits as Lead (3mg/kg), Ni (3mg/kg), Zn (3mg/kg), and Cadmium (3mg/kg) (Health Canada, 2012). The results of recovery study were within the acceptable range verifying the validity of method for the heavy metal analysis as shown in Table-4 below. From the table it can be shown that Lead (Pb) had the highest percentage recovery of 99.27%, followed by Zinc (Zn), 97.38%, then Nickel, 82.05% and lastly Cadmium with percentage recovery value of 79.76%.

Table-3: Mean ± S.D Metal levels in (mg/kg) in all the hair cream samples

Sample	**Mean ± S.D Metal levels in (mg/kg)**			
	Pb	**Cd**	**Ni**	**Zn**
APP	37.600±0.029	0.00±0.000	9.68±0.011	2.27±0.030
TS	0.903±0.032	0.166±0.280	18.93±0.020	14.47±0.060
PX	39.353±0.007	0.00±0.000	154.01±0.017	7.56±0.350
COC	0.133±0.012	0.053±0.009	35.01±0.015	4.60±0.050
SM	44.226±0.036	0.083±0.119	7.03±0.003	5.05±0.040
DAM	0.326±0.004	0.440±0.381	71.34±0.025	2.19±0.011
S8	41.593±0.083	0.020±0.001	53.62±0.020	5.69±0.080
SW	1.573±0.0200	0.106±0.011	31.92±0.011	3.11±0.026
FEM	34.256±0.018	0.006±0.001	173.03±0.005	6.81±0.035
AT	40.676±0.075	0.020±0.003	112.04±0.001	3.48±0.028

Table-4: ANOVA summary table for Heavy metals

Pb	**Cd**	**Ni**	**Zn**
P<0.05	P>0.05	P<0.05	P<0.05

Table-5: Percentage recovery with amount in mg/kg

Metal	Amount in spiked	Amount in unspiked	Amount added	% Recovery
Pb	5.0315	0.0689	5	99.27
Cd	4.120	0.1316	5	79.76
Ni	4.213	0.1107	5	82.05
Zn	5.075	0.2060	5	97.38

$$\textbf{\% Recovery} = \frac{\text{Amount in spiked} - \text{Amount in Unspiked}}{\text{Amount added}} \times 100$$

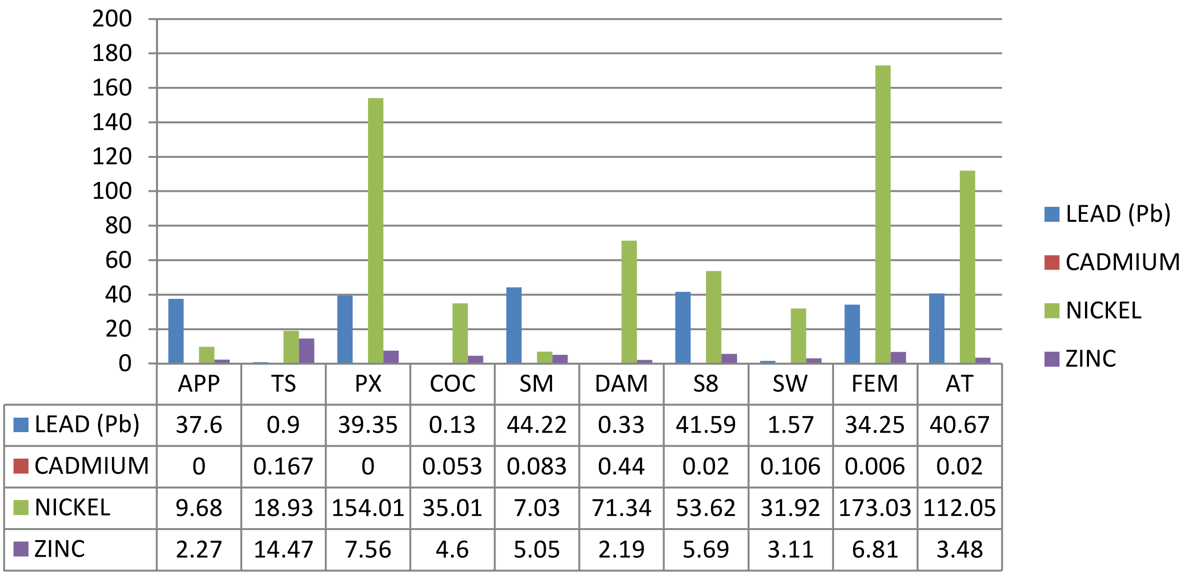

Figure-2: All metal distribution in mg/kg for all hair cream samples

4 CONCLUSION

In the present study, we determined the Cadmium, Lead, Nickel and Zinc in various hair food cosmetics of different brands. Based upon the results, we concluded that most of the heavy metals investigated i.e Pb, Ni and Zn were highly above their maximum permissible limit in most of the hair care cosmetics, only Cd was below the set standard. The continued use of products contaminated with such heavy metals may cause slow release of these metals into the human body and thus show their harmful effects. So the extensive uses of such products should be avoided.

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report.

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