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ASSESSMENT OF SOME HEAVY METALS CONTAMINATION IN SOME BRAND OF CHOCOLATES AND CHEWING GUM AVAILABLE IN KANO METROPOLITANT

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Abstract: **Heavy metals (Pb, Ni, and Cr) were assessed in thirteen different confectionaries which include seven brand of chocolates and six brands of chewing gums commonly found in retail stores and sells on major street in Kano metropolitan. The results indicated concentration of Ni, Cr and Pb in the range of 4.04 – 30.0 µg/g, 3.18 – 12.27 µg/g and 0.13 – 18.75 µg/g in chocolate samples respectively, while the mean concentration of Ni, Pb and Cr in chewing gum samples ranged from 4.04 – 13.8 µg/g, 0.00 – 6.25 µg/g and 0.13 – 16.82 µg/g respectively. Higher concentration of all the studied metals were found in chocolate compared to chewing gum samples. All the confectionaries studied indicated presence of the studied metals (Ni, Pb and Cr) at concentrations which exceeded the permissible limit of 1µg/g prescribed by FAO/WHO (2011) and Poland national standard limit of 0.3µg/g in both chocolate and chewing gum brands studied with exception of Pb in only one sample of chewing gum. Therefore, consumption of those products may likely results to some health implications.**

Keywords: **heavy metals, contamination, Confectionaries.**

1. INTRODUCTION

Food is one of the main sources of heavy metal in take in consumers some heavy metals are essential nutrients (Cu, Ni, Zn) need by our bodies but all of them can be harmful if ingest in heavily metal-contaminated foods or beverage (Gideon *et al*, 2015).Recent trends in food safety issues have generated concern over the presence and level of heavy metals in chocolate and chewing gums. For instance the American environmental safety institute took legal action in 2002 against chocolate manufacture for excessive level of Pb and Cd found in chocolate (Anderson, 2011).Consequently, international legislative bodies, as well as chocolate manufacture countries have introduce new regulations for the protection of the health of their consumers (Ducos and Godula, 2010; Dickso, 2011) European Food Safety Authority (EFSA, 2011)

Heavy, metals enter into human body by ingestion or inhalation and absorption through skin or mucous membrane, when they are not metabolized by the body, get accumulated in soft tissue and become toxic. Due to the industrial revolution, heavy metals easily affect the human health. The presence of relatively high concentration of heavy metal in a consumer product that is marketed to children is an extraordinary concern (Silbergeld, 1997) because children are the most sensitive and vulnerable age group to any kind of contamination in the food chain (Sulbergeld, 1997). While chocolate is regularly eaten for gratification, there are potential health effects of eating chocolate; the uncontrolled consumption of large quantities of any energy rich food such as chocolate without a corresponding increase in activity could increase the risk of obesity and dental complication. Cocoa solid contain alkaloids such as serotonin level in the brain. Some research found that chocolate, consumed in controlled quantity, can lower blood pressure. Candy has a high glycemic index (GL). Which

means that it course a rapid raised in blood sugar level after ingestion. This is of major concern for people with diabetes, but could also be risky to the health of non-diabetics. Many different studies and techniques for heavy metals determination in different stuffs have been reported. Mainly, dry, wet and microwave digestion methods are used to investigate heavy metals levels in cheese; fruits, juices, vegetable, sweet, chocolate, honey, snack, appetizers etc (Soylak *et al*, 2006). The second French TDS (total diet studies). Estimated dietary exposure to 28 essential and non-essential elements in 1319 different food samples (millour *et al* 2011).

1.1 Chocolate and Chewing Gum:

Chocolate is one of the most popular confectioneries consumed by all age groups. Among them children are the most attracted group of consumer of chocolate and at the same time the most vulnerable for toxic metals. Toxic metals accumulate in the body; even consumption of small amount of metals can lead to neurotoxic, carcinogenic and brain disorder (Dias and Wickramasinghe,2013). Chocolate is a sweet confectionary of Theobroma Cacao Seeds. The flavor of chocolate differs depending on the ingredient used and the preparation method of chocolate. Since chocolate are more popular among children, manufacture are very concern about their competitors in the market. Due to this reason chocolate and other confectionaries are sold in a very attractive manner, wrapped in colorful packaging materials.

1.2 Heavy Metals Toxicity:

Toxicity of any metals is governed by several factors; there are interaction with essential metals, formation of metals protein, and complexes chemical form of the metals element, immune status, age and stage of development of the host. Contamination of food products with heavy metals may cause a serious risk for human health because of the consumption of even a small amount of metals can lead to considerable concentration in human body leading to biotoxic effects. The biotoxic effects of heavy metals the refers to the harmful effect of heavy metals to the body when consumed above the bio-recommended limit. The nature of effect could be acute, chronic or sub-chronic, neutrotoxic, concinogenic, mutagenic or tetratogenic (Ochu *et al*, 2012).

1.2.1 Lead and Chromium Toxicity:

Lead absorbed from the food and the atmosphere is retained in tissue like lungs, liver, kidney, and bones. The short term and long term exposure to high level of lead can course brain damage, paralysis, abdominal pain, anemia, renal diseases, memory loss, damage to kidney, reproductive and immune system (Toxicology fact sheet series Food Safety Authority of Ireland, 2009).

Chromium can exist as Cr (III) or Cr (VI). Cr (IV) form is highly toxic. Cr (IV) exposure has been known to be associated with cancer induction in humans, especially bronchial carcinoma and lung cancer (Kim, Ogunfowokm *et al*, 2005;).

1.2.2 Nickel Toxicity:

Nickel is also a well known carcinogen to human, by altering the DNA functions. Even through their DNA- damaging potentials are rather weak, they interfere with the nucleotide and base excision repair at low, nontoxic concentrations. For example both water-soluble Ni (ii) and particular black NiO greatly reduced the repair of DNA. Ni (ii) disturbed the very first step a nucleotide excision repair (Hartmann and Hartwig, 1998).

Many different studies and techniques for heavy metals determination in different food stuffs have been reported in the literature. Concentration of selected metals in candies and chocolate consumed in southern Nigeria ware analysed, the result in chocolate level of Ca, Cd, Ni, Cr, Cu, Pb, Mn, Zn, Fe, Co, and Mg, in candies and chocolate with mean concentration of metals in both confectionaries which ranged between 7.7- 1405 µg/g.(Chukwujundu 2013; Milour *et al*, 2011).

Dias and Wickrymasingle (2013) determined toxic metals in chocolate confectionaries and their wrappers used by the chocolate manufacture in srilendu the result showed Cr concentration in the range 0.78- 388ppm, Ni (not detected - 37ppm), As (not detected), CO(not detected), Sb (not detected-28PPM) and Pb (0.53-6.86ppm).

Assessment of heavy metals contamination (Nickel and Arsenic) using Gf - AAS in local brand chocolate and condies from tiruchirappali India was carried out by Prakish *et al* 2015), it was found that Nickel level in the sample ranged from 0.77 to 5.47 µg/g with an average of 2.75µg/g and arsenic it level range from 0.01 to 4.38 µg/g with an average of 0.81 µg/g, the results showed significant Ni, contamination in the collected confessionary samples which is frequent consumption and courses serious health effect in children and adult as well.

Chukwyjindu *et al(* 2013). Investigates the concentration of selected metals in some Ready- to – eat food consumed in southern Nigeria: Estimation of Dietary intakes and target Hazard Quotients, the concentration of metals ($mgkg^{-1}$) in these ready-to-eat foods are in the range of 2.4 – 2.5 for Cu; 0.1 – 0.8 for Cd; 0.7 – 4.0 for Ni; 0.1 – 53.7 for Fe; 8.9 – 20.0 for Zn; 0.1 – 3.8 for Pd; 5.1 – 14.4 for Mn; 0.83 – 21.4 for Cr and 0.10 – 1.32 for Co. The concentration and estimated intake of Cd, Ni and Pb in some of these food types exceed the permissible limit and tolerable daily intake respectively.

Cost-effective method of analysis for the determination of Cadmium, copper, Nickel and zinc in cocoa beans and chocolates was analysis by Gidon Ramtahal *et al* (2015).

The aim of this study is to assess the concentrations of Lead, Chromium and Nickel in some brand of chocolate and chewing gums commonly available in Kano metropolitan. This is to evaluate the extent to which some commonly consumed Chocolates and Chewing gums in Kano metropolitants conformed to safety guidelines with respect to their heavy metals content.

2. MATERIALS AND METHODS

The water used for sample preparation and cleaning of glass wares in this study was distilled deionized water in order to avoid trace metals contamination. All laboratory glassware and other utensils used were thoroughly washed with a suitable detergent after been socket in an acid bath of 2M nitric acid for at least 24 hours, rinsed in distilled deionized water and dried in an oven at 50^{o}C. All reagent used in this study were of analytical grade unless otherwise stated.

2.1 Preparation of metal stock solution and working standard:

2.1.1 Preparation of 1000 ppm Pb, Ni and Cr solutions:

1.342g of $PbCl_2$, 4.05g of $NiCl_2$ and 2.825g of $k_2Cr_2O_7$ were weighted using analytical balance and transferred into 1 liter volumetric flask separately, 50cm^3 of deionized water was added shaked very well until it dissolved the solute completely, more deionized water added to the mark.

2.1.2 Preparation of metals working standard:

100cm^3 of the 1000ppm stock solution was pipetted into 1000cm^3 volumetric flask and made up to the mark with deionized water to form 100ppm metals stock solution. 0.1, 0.2, 0.4, 0.6, 0.8 and 1.0 cm^3 of the 100 ppm stock solution were transferred into 100 cm^3 volumetric flask and made up to the mark with distilled deionized water to obtain 0.1, 0.2, 0.4, 0.6, 0.8 and 1.0pmm working standard solution.

2.2 Sample Collection:

Thirteen different confectionaries which include seven brands of chocolate and six brands of chewing gums were purchased from retails stories and from hawkers on the major street in Kano metropolitan and stored in polythene bags while the soft chocolate were stored in a refrigerator before subjected to the digestion procedure.

2.3 Digestion of the Chocolate and Chewing Gums Samples:

1g of each of the homogenized chocolate and chewing gums were weighed into 50cm^3 conical flask. 4cm^3 Conc. HNO_3 and 1cm^3 H_2O_2 were added to the flask. The mixture was allowed to digest at 100^{o}C for 10 minutes in microwave oven until solubilisation of the samples were complete. After cooling the flask, the resulting solutions were evaporated to semi dried mass to remove the excess acids. The digested solutions were dilute with distilled ionized water, and then filtered through filter paper. A blank was also prepared using the same procedure but without the sample. All digest sample were analyzed using atomic absorption spectrophotometer (AAS 460 Model). The blank and the calibrated working standard solution were also analyzed in the same way as the samples. Calibration graphs were plotted using the concentration of the standard working solutions against their absorbance.

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3. RESULTS AND DISCUSSION

Table 1: illustrate the result of the mean concentration of Ni, Pb, and Cr in chocolate samples.

The mean concentration of nickel in chocolate samples ranged from 4.04 – 30 µg/g, the highest mean concentration of Ni was found in MR Chocolate samples. The minimum and maximum concentrations of Cr in the analyzed chocolate sample were found to be 3.18 and 12.27 µg/g respectively. The maximum Cr concentration was observed in Co Chocolate samples while the minimum Cr concentration observed in Ar Chocolate samples.

The mean concentration of Pb in the analyzed chocolate samples ranged from 0.13 – 18.75 µg/g, the higher mean concentration of lead was observed in ML sample of chocolate and the lowest mean level concentration of lead found in CO samples.

Table 1: Mean Concentration of Pb, Ni, and Cr in Chocolate Sample (µg/g)

Product Name	Sample Code	Nickel		Chromium		Lead	
		Mean	Range	Mean	Range	Mean	Range
Coco's	Co	13.8	10.23-13.20	12.25	6.14-13.34	0.13	0.05-0.26
Roxy	Rx	16.41	11.20- 15.45	7.73	5.23- 10-72	3.13	2.34-5.64
Armin	Ar	15.76	12.10-14.45	3.18	1.90-4.34	6.25	4.45- 6.87
Cash	Cs	7.29	5.12-6.63	3.18	1.50-3.56	4.69	4.00 – 5.34
My love	ML	30	16.00-28.78	5.45	4.45-5.45	18.75	16. 43-20.12
La seronata	Ls	23.18	21.11-22.78	5.45	3.67-6.67	7.81	6.67 – 8.11
Nemo	Nm	4.04	2.12-3.89	7.37	5.34-8.56	10.94	9.25 – 12.34

Figure 1: show the comparison of metals between different brands of chocolates.

The figure (1) indicated that different brand of chocolate samples contain different or various concentrations of the studied metals. Among the metals studied in the chocolate samples the highest concentration of Ni was found in ML chocolate sample followed by LS, RX, AR, CO, NM and CS which give the following sequential order ML > LS > RX > AR > CO > NM > CS. (figure 1) for Cr the order of the of the mean concentration of Cr is CO> RX> NM > LS > ML > AR > CS while for Pb the order was found to be ML > NM > LS > AR > CS > RX > CO

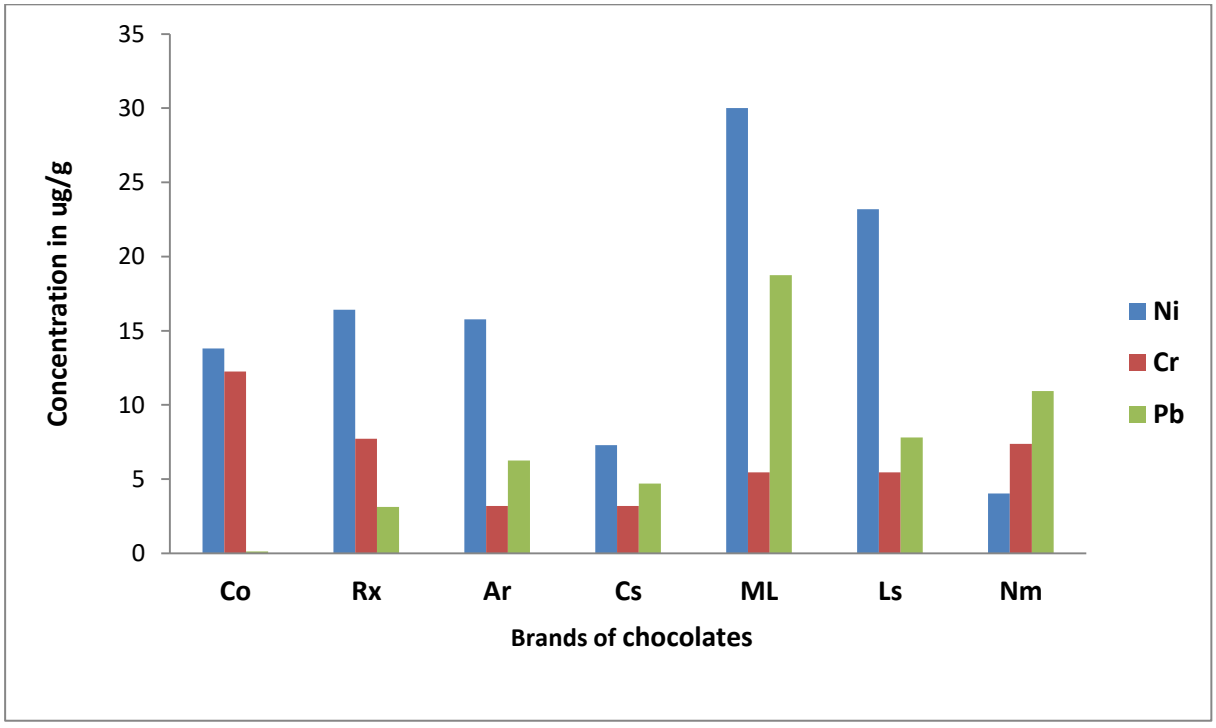

Fig 1: Comparison of metal between different brands of chocolates

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Table 2 : Shows the results of the mean concentration of Ni, Pb, and Cr in chewing gums samples, the mean concentration of Ni in the analyzed chewing gums samples ranged from 4.04 -13.8 µg/g, were the highest concentration was observed in SS samples. The mean concentration of Pb in the chewing gums sample was range from 0.00 – 6.25 µg/g. CT chewing gum sample was found to have the highest concentration of Pb. Also Cr was observed to have the highest concentration in SS and lowest concentration in Tb chewing gum samples.

Table 2: mean concentration of Pb, Ni and Cr in chewing gum sample (µg/g)

Product name	Samples code	Ni		Cr		Pb	
		Mean	Range	Mean	Range	Mean	Range
Big bum	BB	13.80	11.20 - 4.24	3.18	2.14-4.12	6.00	0.00-0.00
Center filled	Cf	9.24	7.45 - 10.23	5.45	5.24-8.45	6.25	3.34-7.50
Crispy	Cp	5.99	3.12 - 6.56	1.36	1.30-2.24	3.13	2.25-4.24
Clips	Cl	4.04	2.40 - 7.08	3.18	3.12-5.42	0.31	0.12-0.30
Time bomb	Tb	11.20	10.24 -12.42	0.13	0.10-0.25	0.00	0.00-0.00
Super star	Ss	11.85	10.21-14.54	16.82	15.20-18.4	4.69	2.45-5.20

Figure 2 indicated that different brand of chewing gum sample contain different concentration of the studied metals. Among the metals studied in the chewing gum samples, the highest concentration of Ni was found in Bg sample following by TB, SS, CT, CR and CP. Which give the following sequential order. TB > SS > CT > CR > CP for Cr the order of the main concentration is SS > CT > CP > Bg > CR > TB, while for Pb the order was found to be CT > SS > CR > CP, but Pb was not found in Bg and TB Chewing gum samples.

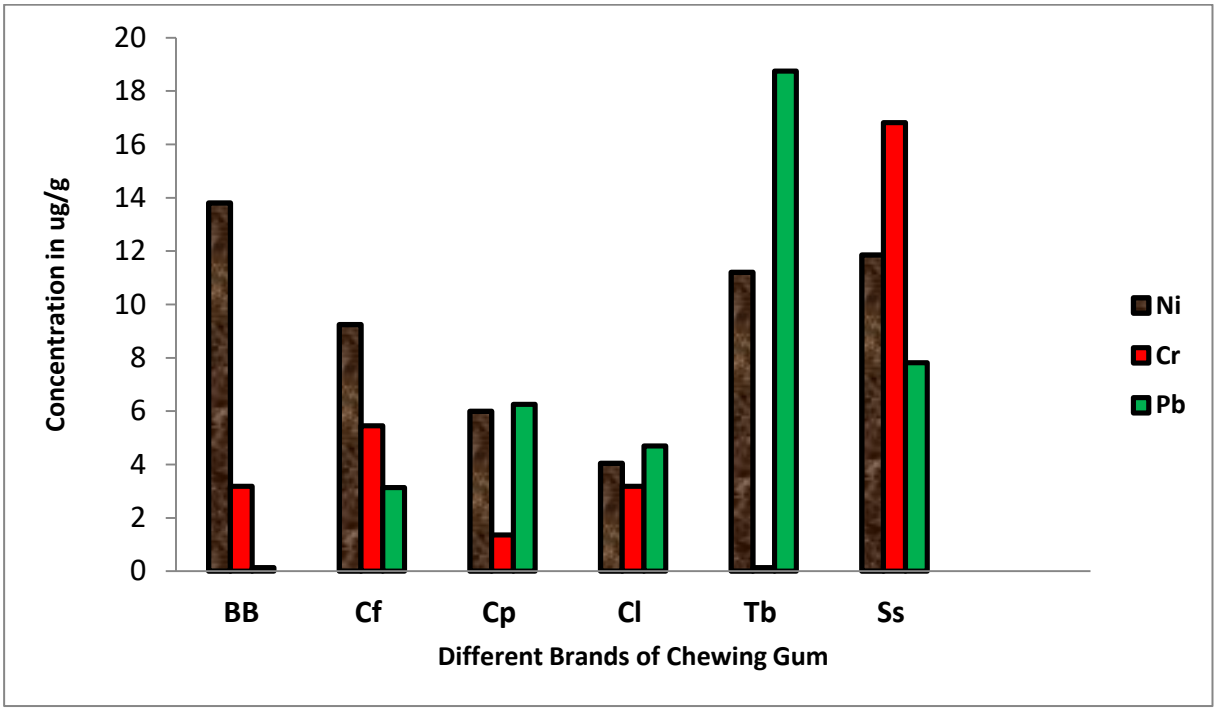

Figure 2: shows comparison of metals between different brands of chewing gum

Table 3: Illustrate the comparison between the standard limits for heavy metals in confectionaries and the present study. Considering the standard permissive limit of the studied metals in the samples, the result (table 3) shows that these samples contained higher concentration of Ni in both chocolate and chewing gums studied. Which are higher than the prescribed limit or exceeded the permissible limit which is 1µg/g for Pb according to FAO/WHO while lower limit was prescribed by the Poland national standard limit (0.3 µg/g). Cr concentration also exceeded the allowable limit of 1 µg/g. So also the mean Ni concentration in both samples of chocolate and chewing gum (15.78 and 9.35 µg/g) were also above the nickel standard level (0.1 – 0.5 µg/g) in the food stuffs, Set by FAO (2001).

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Table 3: Standard Limits for Heavy Metals in Concentration (µg/g)

Regulatory bodies/ Country Limit	Permissible Limits	Metals	Present Study	
			Chocolate	Chewing Gum
FAO/WHO (2011)	1.0µg/g	Pb	7.39µg/g	2.4µg/g
Poland National Standard	0.3µg/g	Pb	7.39µg/g	2.4µg/g
China Standard	1.0µg/g	Cr	6.43µg/g	5.02µg/g
FAO(2001)	0.1 - 0.5µg/g	Ni	15.78µg/g	9.35µg/g

Figure 3: Indicated metal comparison between chocolate and chewing gum samples, the figure showed that chocolate samples contain higher concentration of all the three metals studied, high risk of the heavy metals contamination is associated with chocolate samples more than in chewing gum samples. Although both samples has concentration of the studied metals (Ni, Cr and Pb) higher above the standard limit with the exception of Pb in one sample (i.e Bg Chewing gum).

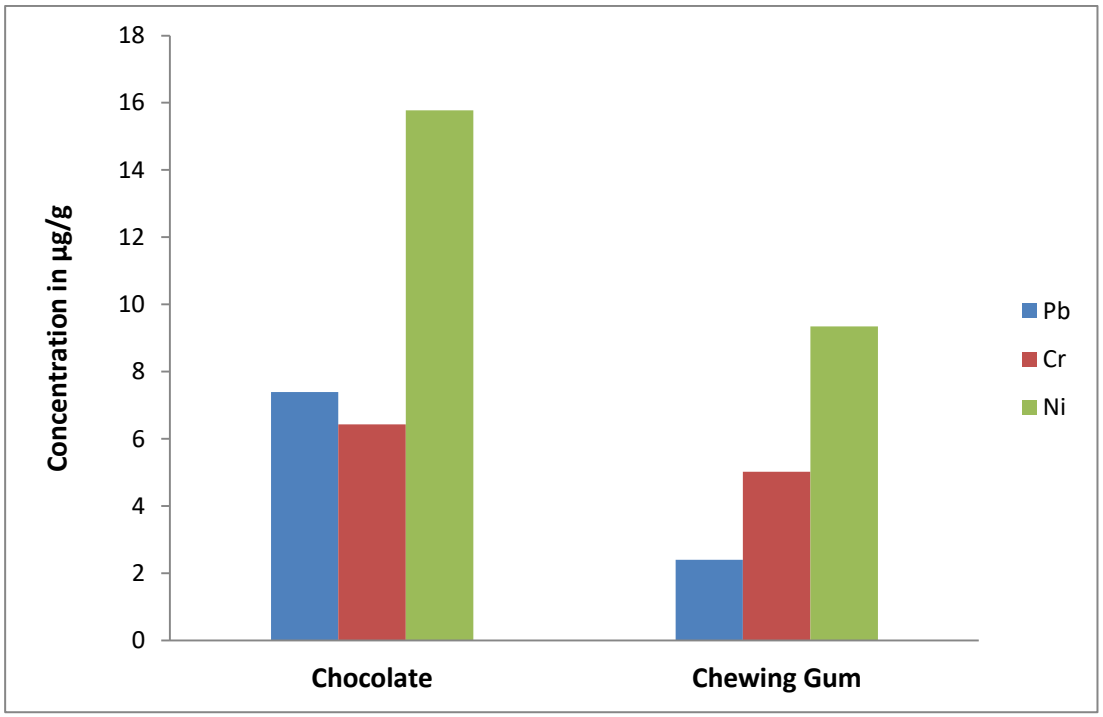

Fig 3: Metals Comparison between Chocolate and Chewing Gum Samples

4. CUNCLUSION

On the bases of the results obtained in this study it can be concluded that Pb, Cr and Ni were detected at higher concentration in the studied chocolates and chewing gums sold in retail stores and by hawkers in Kano metropolitan. Consumption of these products may likely cause health implication. Hence, there is need to exercise caution in Consumption of these products.

5. SUGGESTIONS AND RECOMMENDATIONS

- Laws should be enforced to regulate the consumption of these products due to higher concentration of these metals above the recommended limit.
- It is suggested that people should avoid consumption of such products, more especially children which are more susceptible to these metals contamination
- Public awareness be made to avoid the excess consumption of chewing gums and chocolates which nowadays become a passion without recourse the health implications.

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