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Heavy Metal Determinations in Some Selected Chocolates Marketed in Nigeria

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Abstract:- The study was conducted to determine the concentration of heavy metals in some selected chocolates marketed in Hadejia. The heavy metals analyzed were lead, (Pb), cadmium, (Cd), nickel, (Ni), and chromium, (Cr). Four chocolates samples bought from RDT supermarket of different company with a view to know which product has the highest level of the heavy metals analyzed. Wet digestion method was employed to digest the collected samples. A 10.0 ml mixture of HNO_3 (65%)/H_2O_2 (30%) (v/v) (1:1 ratio) was used to digest the samples and heated at a temperature of 80 ^{0}C for 3 hours on the hot plate. The solutions obtained were diluted with distilled deionized water, and then filtered through Whatman's filter paper. A blank was also prepared using the same procedure but without the sample. All digested sample were analyzed using atomic absorption spectrophotometer (AAS 460 Model). The results obtained showed all the samples analyzed had concentrations of lead, cadmium, and chromium above the recommended limit set by WHO (2011) for food and drinking water. However, the results showed that, the concentrations of nickel found in all the samples were below or within the range set by WHO (2011) for food and drinking water.

Keywords:- *Chocolates & Heavy Metals.*

I. INTRODUCTION

Various food products and beverages are imported into Nigeria and sold through numerous channels, often without thorough investigations into their ingredients. Among these, chocolates stand out as favorites for children and young adults due to their sweetness, delicious taste, affordability, nutritional value, and their use as gifts and souvenirs among loved ones and family members. A wide range of chocolates and candies, featuring different tastes and flavors, are readily available in local grocery stores and supermarkets (Maharjan & Shakya, 2024).

The composition of different types of chocolates varies based on the ingredients and manufacturing processes used. Common ingredients in chocolates include cocoa solids, milk, sugar, liquor, cocoa butter, glucose, vegetable oil, emulsifiers, and buffering agents (Milenur et al., 2024). Chocolates offer a rich blend of carbohydrates, saturated fats, proteins, sugars, vitamins, and essential minerals like zinc, magnesium, phosphorous, calcium, potassium, and iron. Infused with flavonoids and alkaloids such as theobromine and phenyl ethyl amine, chocolates boast antioxidant, anti-inflammatory, anti-depressant, and stimulant properties, contributing to blood pressure reduction (Maharjan & Shakya, 2024).

Food is a primary avenue for heavy metal consumption among individuals. While certain heavy metals like copper (Cu), nickel (Ni), and zinc (Zn) are essential for bodily functions, they can become harmful when consumed in significant amounts from contaminated food or drinks (Sani et al., 2024), whereas lead, cadmium, nickel, arsenic, and mercury are toxic at certain levels. Long term accumulation of cadmium may lead to cancer. Its intake over a long period may accumulate in the kidney and liver because of its long biological half-life causing kidney damage (Godwill et al., 2015). Lead is known to affect humans and animals of all ages, but the effects of lead are most serious in young children (Abubakar et al., 2020). Chromium (Cr) can exist in several oxidation states. Hexavalent chromium (VI) is highly soluble and mobile and is harmful to the skin, liver, kidney, and respiratory organ causing various diseases (Garba & Mustapha, 2018).

Growing concerns about food safety have pinpointed the levels of heavy metals in chocolate and chewing gums. In view of this, the American Environmental Safety Institute initiated legal action in 2002 against chocolate manufacturers due to the excessive levels of lead (Pb) and cadmium (Cd) detected in their products (Garba & Mustapha, 2018).

Heavy metal contamination in chocolates can originate from various sources, one of which is packaging. Chocolates and other confectioneries are often wrapped in vibrant, colorful materials to enhance their appeal. Unfortunately, these packaging materials can contain non-food grade substances and printing inks with toxic elements. A significant risk is associated with the colorful pigments used, such as PbCrO4, an inorganic pigment found in paints and inks (Dias & Wickramasinghe, 2016). Additionally, the diverse ingredients used in the chocolate-making process can also introduce heavy metal pollution (Alamgir et al., 2022).

In view of the above, there is need for through investigation of different brands of chocolates sold with a view to investigate and determine the extent of contaminations of heavy metals to safeguard the life and health of the children and the young people.

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The heavy metal determinations have been widely and effectively employed by common digestion techniques, such as microwave, and conventional acid digestion methods. These digestion techniques require the use of concentrated mineral acids and high temperatures whereas high pressures are required in the case of microwave applications (Jalbani et al., 2009). Due to the complex nature of the target analytes, we employed the conventional acid digestion method to get the target analytes.

II. MATERIALS AND METHODS

A. Chemicals:

Reagents and chemicals used for this research, were of analytical grades and distilled water was used throughout the experiments including preparations, dilutions and rising of apparatus prior to use. HNO_3 (65%, Spectrosol, BDH, UK) and H_2O_2 (30%, Blulux, Laboratories, PLTD, India) were used for sample digestion. Stock standard solutions containing 1000 mg/L of the metals Ni, Cd, Pb and Cr were prepared from $NiCl_2.6H_2O$, Cd $(NO_3)_2$, Pb $(NO_3)_2$, and $Cr_2(SO_4)_3$, respectively of which all were from Sigma Aldrich. Working solutions were prepared from the stock standard solutions of metals by appropriate dilution of the intermediate solution (10 mg/L).

B. Sample Collection:

Four (4) different brands of chocolates were purchased from RDT supermarket in Hadejia metropolitan and stored in polythene bags while the soft chocolate was stored in a refrigerator before subjected to the digestion procedure. The samples were registered and labeled accordingly as BC, GC, SC, and LC for easy identifications.

C. Sample Preparation and Digestion:

The samples collected were dried using microwave oven (GALLENKAP) for about three hours at 70^0C operating temperature and then ground into pieces. Around 20.00 g of each sample was kept until digestion. From this mass of sample, about 1.50 g of triplicate chocolate samples and 1.50 g of candy samples were measured and kept for digestion.

Simple wet digestion technique was employed to digest the collected samples. A 10.0 ml mixture of HNO_3 (65%)/H_2O_2 (30%) (v/v) (1:1 ratio) was used while keeping the temperature at 80 ^{0}C for 2-3 hours on the hot plate. After cooling, the obtained clear solution was allowed to cool for about 10 minutes and then a 15 ml of distilled water was added and mixed. Each replicate samples were transferred into 50ml volumetric flasks using a funnel and Whatman filter paper. The resulting solution was diluted to 50 ml with distilled water.

III. RESULTS AND DISCUSSIONS

Table 1: Metal concentrations in chocolates (mg/g)

Sample ID	Pb	Cd	Cr	Ni
BC	0.05	0.03	0.65	0.07
GC	0.11	0.04	0.47	0.08
LC	0.10	0.05	0.28	0.10
SC	0.17	0.05	0.53	0.06
FAO/WHO RDA	0.015	0.005	0.1	0.1

In all the samples analyzed, lead (Pb), cadmium (Cd), chromium (Cr), and nickel (Ni) were all detected in the samples. The concentrations ranged from 0.005 - 0.17 Pb, 0.03 - 0.05 Cd, 0.28 – 0.65 Cr, and 0.06 - 0.10 mg/g Ni. Sample BC has the least concentrations of Pb, and Cd of 0.05 and 0.03 mg/g respectively while sample SC has the highest concentrations of the metals with 0.17 and 0.05 mg/g respectively. Chromium was higher in all the samples analyzed. The level of metals in the sample are:

Sample BC: Cr > Ni > Pb > Cd,
Sample GC: Cr > Pb > Ni > Cd,
Sample LC: Cr > Pb >= Ni > Cd, and
Sample SC: Cr > Pb > Ni > Cd.

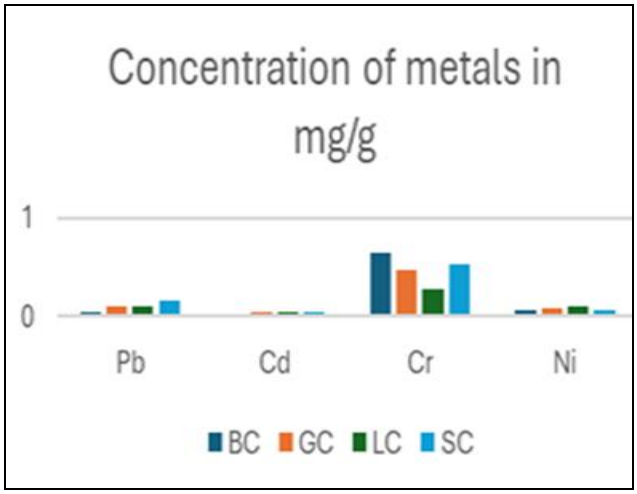

Fig 1: Concentration of Metals in mg/g.

The concentration of lead in all the samples was found to be higher than the recommended limit, this is similar to the results reported by Dauda et al., 2021 which ranges between 0.0194 - 0.0382 mg/g. (Dias & Wickramasinghe, 2016) also detects lead in 3 of 18 chocolates wrappers

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analyzed. Lead contaminations maybe due to industrial activities which dominate the global flux of lead in the environment and have become the major sources of lead in many food items including candies (Dias & Wickramasinghe, 2016)including candies.

Cadmium concentration was found to be low in the sample analyzed though they all exceed the recommended daily intakes set by WHO (2011). The results were in line with the ones reported by Dauda et al., 2021 and Mohammed 2020, that ranges between 0.007 – 0.014 mg/g and 0.1 - 0.2 ppm respectively. Whoever, its contrary with (Milenur et al., 2024) in which there was no Cd detection in both A and B of chocolate wrappers. Presence of cadmium in food may induces toxicity symptoms like gastrointestinal pains, nausea, respiratory distress, diarrhoea, impaired reproductively, kidney damage and hypertension (Jalbani et al., 2009).

Concentration of chromium was higher in all the samples analyzed with 0.65 mg/g found as the highest in sample BC as depicted in figure 1.0. The concentrations were found to exceed the recommended limit sets by WHO (2011), and was found to be much more higher than the one reported by (Dias & Wickramasinghe, 2016) that ranges from 0.38 – 0.40 ppm in brand A chocolates wrappers while no detection found in brand B chocolates. The values were also higher than that reported by Dauda et al 2021 and (Milenur et al., 2024).

Food stuff naturally contains very small amounts of nickel, but its toxicity can lead to lung cancer, nose cancer and prostate cancer (Sani et al., 2024). The level of Ni in the samples ranged between 0.06 – 0.1 mg/g which were all below or withing the recommended daily intakes of WHO (2011). Nickel is found in small quantities in many foodstuffs (0.001-0.01 mg/kg) and in higher concentrations in foodstuffs such as grains, nuts, cocoa products and seeds (up to 0.8 mg/kg) (Ochu et al., 2012).

IV. CONCLUSION

Based on the results obtained in this study it was found that all the chocolate samples analyzed had significant level of heavy metals concentrations that were above or equal to the recommended limits sets by WHO 2011, with great concerned on the toxic metals Pb, and Cd in which the concentrations ranges between 0.05-0.17, and 0.03-0.05, mg/g respectively which are far above the recommended limit of WHO 2011. The values are like the ones found in the literature. With these, I therefore suggest more research to be carried out with a view to assess the health effects of these contaminations in chocolates consumed in Nigeria. Government agencies such as NAFDAC should monitor the food products sold in Nigeria to minimize the contamination level and assure the quality of the products to safeguard public health.

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