

Assessment of some Heavy Metals in selected Chocolate Brands and Bread sold in Kano metropolis, Kano State, Nigeria

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Abstract: Chocolates and breads are widely consumed and can have health benefits, but excessive intake or contamination with heavy metals can be harmful. This study aims to measure levels of lead, cadmium, chromium, and zinc in chocolates and breads sold in Kano City. Three chocolate brands (X, Y, Z) and five bread types (A, B, C, D, E) were obtained and processed through acid digestion to quantify the levels of chromium (Cr), lead (Pb), iron (Fe), cadmium (Cd), and zinc (Zn) by employing atomic absorption spectrophotometry. The measured concentrations of the heavy metals in the chocolate brands varied between 0.02-0.25 mg/kg for Cd, 0.02-0.12 mg/kg for Zn, and 0.08-0.20 mg/kg for Cr. However, lead was not detected in any of the samples analyzed. For the bread samples, the detected concentrations ranged from 0.04-0.15 mg/kg for Cd, 0.60-2.26 mg/kg for Zn, 0.30-0.08 mg/kg for Cr, and 0.02-0.15 mg/kg for Pb. The findings suggest that the levels of heavy metals in the examined chocolate and bread brands fall within permissible limits, thereby presenting no significant health risks upon consumption.

Keywords: Chocolate, Bread, Concentrations, Spectrometry, Acid digestion.

1.0 INTRODUCTION

Heavy metals are defined as metallic or metalloid elements possessing densities exceeding 5 gcm⁻³ and atomic weights ranging from 63.546 to 200.590 g, with a specific gravity of 4.0. When present above the critical threshold, these metals exhibit toxicity to living organisms. Nevertheless, certain heavy metals, including Fe, Mn, Cu, Zn, and Se, are essential at lower concentrations for metabolic functions (Ikem and Egiebor, 2005).

Chocolate is a sweet confection derived from the seeds of *Theobroma cacao*. It is widely consumed across all age demographics (Dias and Wickramasinghe, 2016). Chocolate is frequently consumed for pleasure. While chocolate consumption may confer certain health benefits, excessive intake of energy-dense foods like chocolate without adequate physical activity can elevate the risk of obesity and dental issues. Contamination of food products by heavy metals poses a serious threat to human health. This is because ingesting foods containing even trace amounts of heavy metals can lead to their accumulation in the body, resulting in toxic biological effects (Dias and Wickramasinghe, 2016).

Bread constitutes a staple food of considerable importance, and it can be consumed without undergoing any additional processing (Adejumo *et al.*, 2016). Although awareness has been raised and governmental efforts have been directed toward guaranteeing high-quality bread, bread may nonetheless become contaminated through multiple pathways. The majority of bakeries employ potassium bromate, a potent oxidizing agent, to achieve bread-improving outcomes, including flavor preservation and enhancements in taste and appearance (Adejumo *et al.*, 2016); moreover, it exerts notable influences on food biomolecules such as starch and protein, thereby enhancing the properties of bread (Shanmugavel *et al.*, 2020). For an extended period, the use of potassium bromate was sanctioned as a bread conditioner, given that bromate is transformed into bromide, leaving no detectable residues when subjected to heat during bread manufacturing (Kim *et al.*, 2015).

Heavy metals, by contrast, represent potential environmental contaminants that are capable of entering the food we consume and thereby inflicting harm upon humans (Adeosun and Makanjuola, 2020). Numerous chemical compounds and heavy metals are regarded as toxic contaminants whenever they are present at particular concentrations in food (Rather *et al.*, 2017). The principal pathway by which humans are exposed to heavy metals is predominantly the soil-crop-food route (Adeosun and Makanjuola, 2020). Heavy metals receive particular attention globally owing to their ubiquitous distribution and their toxic consequences even at extremely low concentrations (Hassien, 2022). Elements including Cd, Cr, and Pb are classified as carcinogenic, whereas Fe, Cu, Zn, Ni, and Mn are deemed essential metals; nevertheless, should the concentrations of the latter elements exceed their permissible limits, they are capable of producing toxic effects in humans (AbdAllah, 2017). Nonetheless, because of their chemical and

physiological characteristics, numerous heavy metals prove valuable across many industrial sectors, which amplifies the likelihood of heavy metal exposure.

The objective of this research is to assess the concentrations of selected heavy metals (Pb, Cd, Cr, and Zn) in chocolate and bread samples marketed in Kano City, Kano State, Nigeria.

2.0 MATERIALS AND METHODS

All chemicals employed were of analytical purity and were utilized without additional purification. An atomic absorption spectrophotometer (model 210 VGP) was utilized to identify/quantify heavy metal concentrations in the samples.

2.1 Sample Collection

Three specific chocolate brands, designated as samples A, B, and C, were procured from Sabongari Bata market in Kano City, Kano State. Bread samples were gathered from various bakeries within Kano City, Kano State, and placed in polythene bags for immediate transport to the SLT Research Laboratory for subsequent analysis.

2.2 Sample Preparation by Acid Digestion

2.2.1 Digestion of Chocolates

Each chocolate sample (2 g) was precisely weighed into a 250 ml beaker, followed by the addition of 10 ml of aqua regia (a 3:1 mixture of concentrated HCl and HNO₃). The mixture was heated for 30 minutes, then removed and allowed to cool. Subsequently, 10 ml of 30% hydrogen peroxide (H₂O₂) was added dropwise to prevent any overflow that could result in sample loss. The interior walls of the beaker and the watch glass were rinsed with distilled water. Heating continued until the sample volume was reduced to 5 ml. The resulting solution was then filtered to eliminate insoluble residues and transferred quantitatively to a volumetric flask, where it was made up to the mark (Radojevic and Bashkin, 1999; Akan *et al.*, 2010).

2.2.2 Ashing and Digestion of Bread Samples

Bread samples were placed in porcelain crucibles and subjected to a muffle furnace, where the temperature was increased to 400°C for approximately three hours. After ashing, the samples were removed and cooled in a desiccator for subsequent analysis. An aliquot of 0.5 g from each ashed sample was weighed into a 250 ml beaker. Then, 10 ml of 6 M hydrochloric acid was introduced. The mixture was heated for 15 minutes, then removed and cooled. Subsequently, 1 ml of concentrated nitric acid was added, and the sample was reheated to dryness to dehydrate the silica. Next, 1 ml of 6 M hydrochloric acid was added, followed by 10 ml of distilled water, and the mixture was heated again until dissolution was complete. After cooling, the solution was filtered through Whatman filter paper into a volumetric flask, diluted to the mark with distilled water, and then transferred to a white bottle for further analysis.

2.3 Estimation of Daily Dietary Intake (DIM)

To evaluate the health risk from consuming the studied products, the estimated daily intake (DIM) of each metal was computed using the following equation:

$$DIM = \frac{C_{metal} \times W_{food}}{Bw}$$

Where;

C_{metal} = concentration of heavy metals in the samples in mg/g

W_{food} = daily average weight of the sample consumed (assumed 20 g and 100 g of each sample is taken by children and adult respectively)

B_w = body weight assuming that samples are consumed by children and adult with average body weight of 20 kg and 70 kg respectively)

3.0 RESULTS AND DISCUSSION

The concentrations of heavy metals (Pb, Cd, Cr, and Zn) in selected chocolate brands from Kano City, Kano State, Nigeria markets were investigated using atomic absorption spectrophotometry. The findings are presented in Table 1. Lead was not identified in any of the three chocolate brands analyzed. Cadmium levels ranged from 0.10 to 0.25 mg/L, with brand A exhibiting the highest concentration (0.25 mg/L) and brand B the lowest (0.10 mg/L). Zinc and chromium concentrations ranged from 0.02 to 0.12 mg/L and 0.08 to 0.20 mg/L, respectively. These concentrations exceed those reported by Iwegbue (2011) and Ochu *et al.* (2012). The results align with findings by Dias and Wickramasinghe (2016). All identified or detected heavy metal concentrations in the chocolate brands are within the permissible consumption limits.

Table 1: Mean Concentrations (mg/kg) of Heavy Metals in selected Chocolate brands

Brands	Concentration of heavy metals (mg/kg)			
	Pb	Cd	Zn	Cr
X	NI	0.25	0.02	0.20
Y	NI	0.02	0.10	0.08
Z	NI	0.10	0.15	0.10
WHO Limit	0.24	0.44	1.40	0.11

NI= Not identified

Table 2: Estimated daily intake (DIM) of heavy metals from Chocolates for Children and Adults (mg/kg)

Brands	DIM (mg/kg) for Children				DIM (mg/kg) for Adult			
	Pb	Cd	Zn	Cr	Pb	Cd	Zn	Cr
A	NA	0.25	0.02	0.20	NA	0.288	0.028	0.287
B	NA	0.02	0.10	0.08	NA	0.091	0.143	0.128
C	NA	0.10	0.15	0.10	NA	0.145	0.139	0.145

NA: Not applicable

Heavy metals can contaminate crops and subsequently enter bread products. Flour may also become contaminated if water used for dough preparation contains heavy metals (Hashemi *et al.*, 2017). Moreover, the location of bakeries relative to industrial areas and the types of fuel used are critical factors influencing heavy metal deposition in bread (Shahryari and Mollasadeghi, 2011). Ingestion of these metals can be harmful to human health, particularly at elevated concentrations.

Table 3: Mean Concentration (mg/kg) of Heavy Metals in Bread Samples Compared with WHO standard

Samples	Concentration of heavy metals (mg/kg)			
	Pb	Cd	Zn	Cr
A	0.05	0.04	1.25	0.03
B	0.12	0.09	2.24	0.04
C	0.02	0.14	0.50	0.03
D	0.02	0.06	1.00	0.05
E	0.03	0.12	1.33	0.03
WHO/FAO Limit	0.50	1.50	1.50	9.80

Table 4: Estimated daily Intake of Heavy metals (DIM) from Bread for Children and Adults in mg/kg

Brands	DIM (mg/kg) For Children				DIM (mg/kg) for Adult			
	Pb	Cd	Zn	Cr	Pb	Cd	Zn	Cr
A	0.05	0.04	1.25	0.03	0.075	0.070	1.780	0.045
B	0.12	0.09	2.24	0.04	0.145	0.128	3.300	0.073
C	0.02	0.14	0.50	0.03	0.028	0.189	0.857	0.045
D	0.02	0.06	1.00	0.05	0.025	0.089	1.430	0.087
E	0.03	0.12	1.33	0.03	0.045	0.144	1.872	0.045

The concentrations of heavy metals (Pb, Cd, Cr, Zn) in five locally produced bread brands (A, B, C, D, E) from Kano City, Kano State, were assessed using atomic absorption spectrophotometry. The results are summarized in Tables 3 and 4. Zinc exhibited the highest concentration across all bread samples. Zinc, an essential element for numerous metalloenzymes, was found at the highest levels in all bread samples analyzed (Beliles, 1994; Mohammed *et al.*, 2020). The metal concentrations in samples A and B (Table 2) followed the order Zn > Pb > Cd > Cr, with chromium having the lowest values (0.03 mg/L and 0.04 mg/L, respectively). For samples C and D, the order was Zn > Cd > Cr > Pb and Zn > Cr > Cd > Pb, respectively, with lead showing the lowest concentration (0.02 mg/L). In sample E, the order was Zn > Cd > Cr > Pb, with both Cr and Pb at the lowest level (0.03 mg/L). All measured concentrations were below the permissible limits established by WHO/FAO, indicating that consumption of these bread brands poses no health risk. Most heavy metals are toxic and often carcinogenic, as they tend to accumulate in human visual and sensory organs, potentially leading to cancer. Therefore, bread intended for consumption must adhere to WHO safety standards.

4.0 CONCLUSION

Samples of chocolate brands and bread were analyzed for levels of some heavy metals (Pb, Cd, Zn, and Cr). The results of this studies revealed that the studied heavy metals were found to be below the FAO/WHO standards. This implies that the consumption of the studied brands of bread pose no health risk or hazards.

SUGGESTIONS AND RECOMMENDATIONS

1. Laws should be enforced to regulate the consumption of these products due to higher concentration of these metals above the recommended limit.
2. It is suggested that people should avoid consumption of such products, more especially children which are more susceptible to these metals contamination.
3. 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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AUTHOR CONTRIBUTIONS

All authors contributed toward data analysis, drafting and critically revising the paper and agree to be accountable for all aspects of the study.

DISCLOSURE

We declared no conflicts of interest in this research.

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