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Quantitative evaluation of potassium bromate and some heavy metals in selected bread samples produced in Sokoto State, Nigeria

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Abstract
Bread is among the stable and essential food consumed widely amongst all socioeconomic groups in Nigeria. Fourty-Six (46) different bread products were sampled and analysed, aimed at evaluating the level of potassium bromate in the bread loaves and improvers, as well as to determine the level of selected vitamins (A and E) and heavy metals in the bread products. The result revealed the presence of potassium bromate in the entire bread samples and improvers analysed. Samples with highest concentration of potassium bromate were observed to have lowest concentration of vitamins A and E and vice versa. The heavy metal evaluated are Nitrite (NO_2^-), Lead (Pb), Cadmium (Cd), Cupper (Cu), Zinc (Zn) and Iron (Fe). The result showed that all the bread samples analysed contained NO_2^- at the mean level of ranges from 0.026±0.008mg/kg to 0.397±0.009mg/kg, while Thirty (30) samples contained Pb at the range from 0.147±0.095mg/kg to 12.355±0.022mg/kg. Eight (08) samples are also shown to contain Cadmium (Cd) within the range of 0.025±0.006mg/kg to 0.868±0.099mg/kg while only fourteen (14) bread samples had Cupper (Cu). The level of Zinc (Zn) ranges from 0.009±0.000mg/kg to 1.468±0.021mg, but no quantity of Iron (Fe) was detected in any of the bread sample analysed. Some of the values for Pb and Cd are within the permissible limit, while Cu and Zn content in all the samples are below the permissible limit. The findings of this study showed that potassium Bromate degrades vitamins A and E in the bread whereas the concentration of potassium bromate in the bread samples observed may be due to the bread improvers used by the bread baker because of the high concentration of the chemicals observed in all the improvers analysed.

Keywords: bread, potassium bromate, vitamins A and E, improvers, heavy metals

Introduction

Bread is one of the essential foods consumed extensively among all socioeconomic groups in Nigerian, due to its availability and convenience in consumption (Alli *et al.*, 2013) [1]. It is prepared from dough of flour and other ingredients (Magomya *et al.*, 2013) [2], through a number of processes including milling, mixing, fermenting, moulding and baking (Emeje *et al.*, 2010) [3]. Other ingredients for its preparation include water, sugar, salt, improvers and preservatives in some cases. Bread supplies a significant portion of the nutrients required for growth, maintenance of health and well-being. It is an excellent source of proteins, vitamins (such as Thiamin-B1, Niacin-B3, Folic acid-B9, Vitamin E and to some extent vitamin A), minerals, fibre and complex carbohydrate. It is also low in fat and cholesterol.

Due to disparity in the composition of flour, other additives or enhancing agents (bread improvers) are added to the formulation for its enhancement during mixing, extensibility for moulding, increase in fermentation of bread in the oven and to also increase the quantity of loaf and its texture (Emeje *et al.*, 2010) [3]. Potassium bromate is one of the bread improvers used by the bakers, even though studies by Alli *et al.* (2013) [1]; Magomya *et al.* (2013) [2]; Emeje *et al.* (2010) [3]; Oloyede and Sunmonu, (2009a) [4]; Abubakar *et al.* (2008) [5] have revealed its detrimental health effect thereby necessitating its ban by the food regulatory Agencies of the world including NAFDAC and others. Beside the bread consumers, factory workers are also known to get poisoned with potassium bromate through inhalation due to its hepatotoxic and nephrotoxic effect as reported by Oloyede and Sunmonu (2009) [4].

Potassium bromate is a strong oxidizing agent during the fermentation and baking process and it's commonly used as flour enhancing agent in Nigeria (Emeje *et al.*, 2010) [3]. Emeje *et al.* (2010) [3] stated that the use of potassium bromate has been manipulated by the producers of bread improvers and flour millers in order to get high patronage from the bakers due to its efficient oxidizing agent.

Potassium bromate affects the dietetic value of bread by degrading essential vitamins and fatty acid. Emeje *et al.* (2015) [6] reported that the concentration of vitamins B1, B2 and B3 in some Nigerian bread are small but predominantly rich in Vitamin A due to the mandatory fortification process mandated by the regulatory Agencies on food vehicle which flour is among them.

Mineral elements are significant to daily needs of the body and bread is one of the major foods that provide 50% to 90% of the total calories and proteins required by the human biological system (Jahed, 2005) [7]. Specific attention are given to heavy metals worldwide due to their common nature and are the most noxious elements because of their biodegradability and potential to cause poisonous impacts even at minute quantity (Tchounwou *et al.*, 2012) [8]. Bread contaminated with heavy metals are one of the major route for human exposure to the heavy metals and these

contamination could arise due to bioaccumulation of heavy metals in wheat or flour (Heyes, 1997) [9] particularly wheat that may have been grown on farmlands with high concentration of heavy metals (Onianwa *et al.*, 2001) [10], or may be from irrigation water which are polluted by metals (Christophe *et al.*, 2009). Heavy metals introduction in bread production may also be from the equipment or utensils used during bread processing (Onianwa *et al.*, 2001; Jahed, 2005) [7, 10] or from environments where bakeries are situated or from air and baking fuel such as heavy oil, light oil (diesel) and electricity and in some few cases from packaging material and environmental contamination which may occur (Heyes, 1997) [9]. Furthermore, Khaniki *et al.* (2005) [11] reported that all these factors contribute significantly to the introduction of heavy metals in the bread product.

Heavy metals such as Cd, Cr and Pb are known to be carcinogenic, while Fe, Cu, Zn, Ni and Mn are essential metals, and if their levels are higher than the permissible limits may leads to toxic effects in humans (Gulfrazi *et al.*, 2003) [12]. Lead (Pb) and Cadmium (Cd) are non-essential element for almost all living things and are among the ceaselessly used element in many industrial centres thereby getting into wheat flour and then bread easily (Khaniki *et al.*, 2005) [11]. Onianwa *et al.* (2001) [10] revealed that all categories of grains including wheat may hold heavy metals such as iron (Fe), manganese (Mn), magnesium (Mg), copper (Cu), and zinc (Zn) as a result of environmental situation mostly weather during cultivation or rain. The use of chemical fertilizer and sewage sludge during cereals cultivation will significantly increase the levels of NO_2^-, Pb, Zn, and Cd (El-Nahhal, 2018) [13].

Several studies have been conducted on the potassium bromate and heavy metals contents in the bread samples in various places across the globe few among them are: Gulfrazi *et al.* (2003) [12]; Oloyede and Sunmonu (2009) [4]; Obunwo and Konne (2014) [14]; Oyekunle *et al.* (2014) [15]; Irogbeyi *et al.* (2019) [16]; Aletan (2020) [17]; Suleiman *et al.* (2020) [18] and Ufuoma *et al.* (2020) [19] amongst others. However, most of the documented studies focused on the determination of potassium bromate and heavy metals in the bread samples without given much consideration to the raw materials including bread improver used by the baker. Study by Magomya *et al.* (2020) [20] is among the few studies conducted in Nigeria that examined the presence of potassium bromate in flour and his findings revealed the presence of potassium bromate in all the flour products analysed. Although Abubakar *et al.* (2008) [5] has conducted similar study in Sokoto State, but his study was limited to the presence of potassium bromate in bread products baked and consumed in Sokoto metropolis.

Sokoto State has a population of 3,696,999 people (2006 National Population Figure) with a land area of 28,232.37sq kilometres, located between longitudes 11º 30' to 13º 50' East and latitude 4º to 6º North. It is bordered in the North by Niger Republic, Zamfara State to the East and Kebbi State to the South and West. Preliminary assessment showed that there are about two hundred and fifty (250) bakeries in the state, with some operates under poor sanitary condition and lack certification from the regulatory body (NAFDAC).

The findings of the studies conducted in many parts of the world and Nigeria in particular necessitated the need for this study on the potassium bromate content, vitamins (A and E) and heavy metals in the bread products produced and sold in Sokoto State. The State has a lot of industrial and human activities coupled with lack of portable water supply particularly in rural areas. Therefore, this study was aimed to evaluate the level of potassium bromate in the bread loaves and improvers, as well as to assess the level of some heavy metals and vitamins in the bread loaves with a view to ascertain the bread product that conformed to standard safety regulations and to determine the levels of exposure of these metals by the people of the State who predominantly consumed bread as one of their major stable food.

Materials and Methods

Sample Collection

A total of Fourty Six (46) different bread samples were selected and sampled for this study. Two (2) bread samples were selected and analysed from each of the 23 Local Government Areas (LGAs) of Sokoto State, Nigeria. The samples used for this study were most commonly consumed in their respective LGA.

Sample Preparation

A circular sample of 2cm diameter from the center of each bread sample was taken and dried in an oven for 72 hours at 55ºC; the crust was ground to a fine powder with mortar and pestle according to method of Ekop *et al.* (2008)[21]. Consequently, 5g of each powdered sample was weighed into a clean 250ml beaker and 10ml of distilled water was added. The mixture was shaked and filtered using Whatman filter paper. The residue was discarded leaving only the filtrate which was used for the analysis.

Methods

Potassium bromate was qualitatively determined using method of Ojeka *et al.* (2006) [22] while quantitative determination was done using spectrophotometric method described by El Harti *et al.* (2011). The absorbance of the sample was measured using spectrophotometer (Spec. 721A, Jefferson Ltd, USA) at 452nm to determine the quantity of potassium bromate present. The concentration of potassium bromate was calculated using a linear regression curve obtained from the working standard. The analysis of each sample was done in a triplicate, mean and standard deviation (SD) was obtained.

Determination of vitamins A and E was done using the methods of Bassey *et al.* (1946) and Baker and Frank (1968) respectively.

Furthermore, method of Oyekunle *et al.* (2014) [15] was adopted for the determination of heavy metals such as Nitrite, Iron, Zinc, Copper and cadmium. Exactly, 1.0g of each powdered bread sample was weighed and transferred into a 100ml Teflon beaker; followed by addition of 10ml concentrated nitric acid (HNO_3) and the content was mixed gently and placed on a thermostatic heating mantle at 120-150ºC for about 1 hour. Subsequently, 2ml of perchloric acid ($HClO_4$) was added and digested further for about 30 minutes. The mixture was removed from the heating mantle and the digested sample was quantitatively transferred into 25ml volumetric flask and filled to the mark with double distilled water in readiness for the analysis. The digested sample solutions were used for determination of the heavy metals using Flame Atomic Absorption Spectrophotometer (Bulk Model 205). The standards were prepared from individual 1,000ppm stock solution of the respective metals prepared from their respective salts.

Statistical Analysis

The results of the study are presented as Mean±SD. Statistical analysis was done using Microsoft Excel.

Results and Discussion

Results

The result of potassium bromate substance, vitamins A and E are presented in a Table 1. The result of the study showed that all the bread samples analysed contained potassium bromate. The quantity of potassium bromate in each of the sample analysed was higher than the FDA's and NAFDAC's permissible limit of 0.02mg/kg (Ekop *et al.*, 2008) [21] but lower than the permissible limit approved by China and Japan of 50mg/kg and 10mg/kg respectively as reported by Johnson *et al.* (2013) [23]. The highest quantity of potassium bromate was observed in samples O2, N1 and E2 containing 0.674 ± 0.020mg/kg, 0.659 ± 0.003mg/kg and 0.655± 0.003m/kg respectively. Furthermore, lowest amount of 0.033±0.002mg/kg, 0.062±0.002mg/kg and 0.083±0.002mg/kg was detected in samples I1, B1 and F2 respectively. The bread sample with the highest concentration of $KBrO_3$ (0.674 ± 0.020mg/kg) is multiple times higher than the acceptable limit (0.02mg/kg) while the sample with the lowest quantity (0.033±0.002mg/kg) was slightly above the acceptable limit. Additionally, samples with highest concentrations of $KBrO_3$ (Samples O2, N1 and E2) was observed to have lowest concentration of vitamins A and E, hence potassium bromate may degrade the vitamins. Likewise, highest quantity of vitamins A and E was observed in samples with lowest concentration of $KBrO_3$ (samples I1, B1 and F2).

Table 1: Concentration of Potassium Bromate and Vitamins A and E in Bread Samples in Sokoto State.

S/No	Sample No	$KBrO_3$ (mg/kg)	Vitamin A (mg/dl)	Vitamin E (mg/dl)
1.	A1	0.114 ± 0.003	2.36 ± 0.06	22.47 ± 0.22
2.	A2	0.109 ± 0.004	2.08 ± 0.03	35.40 ± 0.38
3.	B1	0.062 ± 0.002	3.13 ± 0.04	63.56 ± 0.11
4.	B2	0.273 ± 0.002	2.18 ± 0.06	37.60 ± 0.22
5.	C1	0.146 ± 0.004	2.28 ± 0.04	52.98 ± 0.22
6.	C2	0.108 ± 0.001	2.59 ± 0.07	43.69 ± 0.00
7.	D1	0.389 ± 0.003	2.06 ± 0.06	37.98 ± 0.11
8.	D2	0.112 ± 0.003	2.26 ± 0.07	35.15 ± 0.22
9.	E1	0.093 ± 0.003	1.96 ± 0.13	38.04 ± 0.38
10.	E2	0.655 ± 0.003	1.84 ± 0.04	20.27 ± 0.22
11.	F1	0.093 ± 0.003	2.18 ± 0.22	42.94 ± 0.38
12.	F2	0.083 ± 0.002	2.91 ± 0.02	59.07 ± 0.22
13.	G1	0.090 ± 0.004	2.52 ± 0.07	29.38 ± 0.19
14.	G2	0.159 ± 0.003	2.52 ± 0.07	50.72 ± 0.39
15.	H1	0.241 ± 0.003	2.28 ± 0.04	22.47 ± 0.22
16.	H2	0.291 ± 0.003	2.22 ± 0.13	45.07 ± 0.11
17.	I1	0.033 ± 0.002	3.34 ± 0.51	64.02 ± 0.19
18.	I2	0.383 ± 0.004	2.83 ± 0.03	25.11 ± 0.22
19.	J1	0.211 ± 0.003	2.89 ± 0.04	43.94 ± 0.11
20.	J2	0.331 ± 0.001	2.04 ± 0.04	41.05 ± 0.19
21.	K1	0.240 ± 0.003	2.08 ± 0.03	48.71 ± 0.11
22.	K2	0.330 ± 0.016	2.83 ± 0.31	45.07 ± 0.11
23.	L1	0.279 ± 0.004	2.59 ± 0.19	51.85 ± 0.11
24.	L2	0.234 ± 0.003	2.89 ± 0.13	23.29 ± 0.04
25.	M1	0.327 ± 0.002	2.71 ± 0.07	22.79 ± 0.19
26.	M2	0.436 ± 0.002	2.44 ± 0.04	21.97 ± 0.66
27.	N1	0.659 ± 0.003	1.84 ± 0.04	14.47 ± 0.22
28.	N2	0.324 ± 0.008	2.79 ± 0.12	21.15 ± 0.47
29.	O1	0.432 ± 0.004	2.62 ± 0.04	47.58 ± 0.22
30.	O2	0.674 ± 0.020	1.15 ± 0.06	12.49 ± 0.11
31.	P1	0.591 ± 0.003	2.14 ± 0.03	26.11 ± 0.47
32.	P2	0.303 ± 0.003	2.73 ± 0.16	21.15 ± 0.47
33.	Q1	0.290 ± 0.009	2.75 ± 0.13	35.72 ± 0.11
34.	Q2	0.287 ± 0.013	2.63 ± 0.14	35.91 ± 0.39
35.	R1	0.368 ± 0.009	2.56 ± 0.07	42.37 ± 0.19
36.	R2	0.440 ± 0.009	2.60 ± 0.06	37.22 ± 0.22
37.	S1	0.155 ± 0.011	2.62 ± 0.09	25.74 ± 0.22
38.	S2	0.216 ± 0.006	2.81 ± 0.09	42.62 ± 0.58
39.	T1	0.267 ± 0.003	2.08 ± 0.03	35.40 ± 0.38
40.	T2	0.340 ± 0.007	2.04 ± 0.19	38.04 ± 0.38
41.	U1	0.327 ± 0.014	2.46 ± 0.19	42.94 ± 0.38
42.	U2	0.377 ± 0.002	2.91 ± 0.18	53.29 ± 0.19
43.	V1	0.184 ± 0.003	2.83 ± 0.03	21.15 ± 0.47
44.	V2	0.375 ± 0.006	2.91 ± 0.18	42.37 ± 0.19
45.	W1	0.402 ± 0.006	3.13 ± 0.04	23.29 ± 0.04
46.	W2	0.372 ± 0.047	2.79 ± 0.12	26.11 ± 0.47

Key: Values are expressed as mean ± standard deviation, $KBrO_3$: Potassium bromate

Table 2 showed the concentration of $KBrO_3$ in Five (5) different bread improvers used by bread bakers in the State. The result of the study showed that all the improvers contained high concentration of potassium bromate. The highest concentration was observed in sample D, C and E having contained 0.533±0.003, 0.452±0.002 and 0.445±0.002mg/kg respectively.

Table 2: Concentration of Potassium Bromate in Some Bread Improvers Sold in Sokoto State.

S/No	Sample No	$KBrO_3$ Conc. (mg/kg)
1.	A	0.405 ± 0.003
2.	B	0.361 ± 0.048
3.	C	0.452 ± 0.002
4.	D	0.533 ± 0.003
5.	E	0.445 ± 0.002

Key: Values are expressed as mean ± standard deviation, $KBrO_3$: Potassium bromate

Similarly, the results of heavy metals such as Nitrite (NO_2^-), Lead (Pb), Cadmium (Cd), Cupper (Cu), Zinc (Zn) and Iron (Fe) in the bread samples was presented in Table 3. The mean level of NO_2^- ranges from 0.026±0.008mg/kg to 0.397±0.009mg/kg. The result showed that sample C2, A1 and B1 contained highest concentration of nitrite (NO_2^-) with 0.397±0.009mg/kg, 0.387±0.006mg/kg and 0.367±0.007mg/kg respectively while the lowest concentration of 0.026±0.008mg/kg, 0.027±0.001mg/kg and 0.030±0.004mg/kg was observed in samples O2, V1 and N1 respectively. Furthermore, out of Fourty Six (46) samples analysed, the result showed that Thirty (30) bread samples contained Lead (Pb) with only seven (07) samples having Pb within a permissible limit of 0.2 to 2.5mg/kg in a food. The result also showed that samples D2, S1 and L2 have the highest concentration of Pb with 12.355±0.022mg/kg, 11.290±0.242mg/kg and 10.570±0.274mg/kg respectively while the lowest level of 0.147±0.095mg/kg was detected in sample I2. Eight (08) samples were shown to contain Cadmium (Cd) within the range of 0.025±0.006mg/kg to 0.868±0.099mg/kg. From the result obtained four (04) samples out of eight (08) had Cd within the permissible limit of 0.05mg/kg. Similarly, the finding of the study revealed that fourteen (14) bread samples had Cupper (Cu) though below the permissible limit of 10mg/kg. The highest Zinc (Zn) level in the bread samples analysed was observed in samples D1 with a level of 1.468±0.021mg while the lowest concentration was observed in sample T1 having contained 0.009±0.000mg/kg which are all below the acceptable limit of 50mg/kg. No amount of Iron (Fe) was detected in any of the bread samples analysed.

Table 3: Concentration of Heavy Metals in Bread Samples in Sokoto State.

S/No	Sample No	Nitrite (NO_2^-)	Lead (Pb)	Cadmium (Cd)	Cupper (Cu)	Zinc (Zn)	Iron (Fe)
1.	A1	0.387±0.006	-	-	0.182±0.012	0.680±0.060	-
2.	A2	0.157±0.006	-	-	1.684±0.032	-	-
3.	B1	0.367±0.007	3.046±0.111	-	0.052±0.013	-	-
4.	B2	0.113±0.004	-	0.750±0.089	0.001±0.000	-	-
5.	C1	0.198±0.009	7.147±0.081	-	0.092±0.027	-	-
6.	C2	0.397±0.009	-	-	1.067±0.040	0.191±0.001	-
7.	D1	0.248±0.010	-	-	-	1.468±0.021	-
8.	D2	0.135±0.020	12.355±0.022	-	0.041±0.011	-	-
9.	E1	0.198±0.118	6.759±0.050	-	1.136±0.069	-	-
10.	E2	0.142±0.005	0.242±0.076	0.349±0.049	0.040±0.054	0.659±0.099	-
11.	F1	0.226±0.008	7.314±0.008	-	-	1.462±0.060	-
12.	F2	0.159±0.009	6.072±0.402	-	0.158±0.054	-	-
13.	G1	0.156±0.004	10.210±0.242	-	-	-	-
14.	G2	0.132±0.009	-	0.868±0.099	-	-	-
15.	H1	0.092±0.004	7.608±0.163	-	-	1.159±0.020	-
16.	H2	0.168±0.004	7.515±0.275	-	-	0.859±0.047	-
17.	I1	0.213±0.002	8.616±0.245	-	-	-	-
18.	I2	0.198±0.009	0.147±0.095	-	0.149±0.019	-	-
19.	J1	0.134±0.000	-	-	-	0.333±0.045	-
20.	J2	0.117±0.003	-	-	-	0.273±0.022	-
21.	K1	0.274±0.002	-	-	-	-	-
22.	K2	0.122±0.004	-	-	-	-	-
23.	L1	0.261±0.003	9.129±0.356	-	0.181±0.084	-	-
24.	L2	0.120±0.004	10.570±0.274	-	0.059±0.266	-	-
25.	M1	0.059±0.006	3.554±0.208	-	-	0.286±0.011	-
26.	M2	0.172±0.002	-	-	-	-	-
27.	N1	0.030±0.004	0.263±0.019	0.778±0.469	-	0.394±0.010	-
28.	N2	0.043±0.004	0.373±0.077	-	-	-	-
29.	O1	0.053±0.004	4.341±0.216	-	-	-	-
30.	O2	0.026±0.008	-	-	-	-	-
31.	P1	0.155±0.004	3.841±0.633	0.049±0.002	-	0.020±0.010	-
32.	P2	0.171±0.003	12.839±0.232	-	-	1.285±0.031	-
33.	Q1	0.159±0.009	-	0.025±0.006	-	-	-
34.	Q2	0.121±0.003	4.138±0.192	-	-	-	-
35.	R1	0.140±0.005	8.248±0.109	-	-	0.158±0.160	-
36.	R2	0.217±0.005	-	-	-	0.925±0.115	-

37.	S1	0.344±0.004	11.290±0.242	-	-	0.020±0.010	-
38.	S2	0.086±0.004	0.720±0.255	0.232±0.026	-	-	-
39.	T1	0.028±0.009	7.671±0.225	-	-	0.009±0.000	-
40.	T2	0.198±0.009	0.586±0.126	-	0.798±0.280	-	-
41.	U1	0.341±0.003	6.758±0.200	0.025±0.006	-	0.278±0.030	-
42.	U2	0.089±0.002	-	-	-	-	-
43.	V1	0.027±0.001	-	-	-	-	-
44.	V2	0.206±0.002	3.117±0.243	-	-	-	-
45.	W1	0.157±0.002	0.441±0.171	-	-	0.146±0.042	-
46.	W2	0.104±0.000	8.744±0.091	-	-	0.178±0.014	-

Key: Values are expressed as mean ± standard deviation, - : Not detected.

Discussion

The result of our finding revealed that all the bread samples analysed contained potassium bromate. The concentration of potassium bromate was found to be significantly higher than the permissible limit of 0.02mg/kg approved by the United State Food and Drug Agency (FDA) (Ekop *et al.,* 2008; Obunwo and Konne, 2014) [24, 21, 14] though this acceptable limit was withdrawn by the joint committee of FAO/WHO due to the long term toxicity and carcinogenic effect of potassium bromate which was proved through numerous *in vitro* and *in vivo* studies conducted across the world which revealed renal cell tumours in hamsters (Oyekunle *et al.,* 2014) [15] and this necessitated its banned in many countries around the world (Oloyede and Sunmonu, 2009) [4]. In Nigeria, the country's apex drug and food regulatory Agency; the National Agency for Food and Drug Administration and Control (NAFDAC) has banned the use of potassium bromate in bread since 2003 due to its deleterious health effect (NAFDAC, 2003; Emeje *et al.,* 2015; Airaodion *et al.,* 2019) [25, 6, 26], hence the Agency described the use of the chemical as a great offence and violation of its regulation, thus stipulated a penalty for the offenders.

Potassium bromate was reported to induce renal oxidative stress, thereby causing renal failure, methaemoglobinaemia and kidney cancer (Ahmad *et al.,* 2013) [28]. Similarly, Ahmad *et al.* (2015) [29] reported that potassium bromate causes oxidative damage to the mammalian DNA and has the ability to cause bone marrow suppression with selective megakaryocyte depression. Also, Ahmad *et al.* (2013) [28] and (2015) [29] revealed that $KBrO_3$ is injurious to many tissues of the body especially those of central nervous system (CNS) and has a great ability to induce toxicity in numerous organ of humans and experimental animals, and the main target of this compound is always kidney.

Apart from the hepatotoxic, neurotoxic, nephrotoxic, mutagenic and carcinogenic effect of $KBrO_3$ as broadly reported, several studies also revealed that it causes abdominal pain, diarrhea, nausea, vomiting, hearing loss, cough, sore throat, bronchial, hearing and ocular impairment (Emeje *et al.,* 2015) [6].

The finding of our study is in conformity with the numerous studies carried out in different location of the country. In the Federal Capital Territory (FCT) of Nigeria, studies were conducted by Alli *et al.* (2013) [1] and Emeje *et al.* (2015) [6] where they sampled and analysed 20 and 26 different bread samples respectively and the result of their studies revealed presence of potassium bromate in all the bread products. Likewise, in Northwestern region of the country numerous studies were carried out by several researchers such as Abubakar *et al.* (2017) [30] where they sampled 150 bread products in Kano metropolis and all the samples were found to contain potassium bromate. Different studies were conducted in different location of Kaduna State by Ojeka *et al.* (2006) [22]; Magomya *et al.* (2013) [2] and Olabimtan *et al.* (2014) [31]; were their findings revealed the presence of potassium bromate in all the bread samples and equally in Kebbi State, Ufuoma *et al.* (2020) [19] reported that all the 35 bread samples analysed for the presence of potassium bromate produced positive result. Abubakar *et al.* (2008) [5] sampled 15 bread samples in Sokoto metropolis and all of them contained potassium bromate. Similar result was also reported in Katsina State by Shuaibu and Ibrahim (2013) [32] where they sampled 20 bread samples and all were considered unsafe for human consumption due to high concentration of potassium bromate. Studies by Oyekunle *et al.* (2014) [15]; Akpambang and Onifade (2019) [33] and Aletan (2020) [17] conducted in Ile-Ife metropolis (Osun State), Akure (Ondo State) and Lagos State respectively reported that all the bread samples analysed had potassium bromate. In two (2) separate and documented studies conducted in Ibadan and Ogbomoso metropolitan areas of Southwestern Nigeria by Airaodion *et al.* (2019a&b) [26, 27] showed that all the bread samples analyzed contained potassium bromate. In southeastern part of the country, Irogbeyi *et al.* (2019) [16] sampled and analysed 32 different bread samples in Aba metropolis and the results of the analysis revealed that all the bread samples contained potassium bromate. Likewise another study was carried out by Emeje *et al.* (2010) [3] in Enugu State where they sampled and analysed 23 bread samples and only 2 samples are negative. Moreover, Chike *et al.* (2013) [34] conducted similar investigation in Awka of Anambra State and observed all the bread samples analysed contained potassium bromate. Furthermore, in separate studies conducted in different locations of Port Harcourt and its Environs alone by Obunwo and Konne (2014) [14]; Naze *et al.* (2018) [35]; Naze *et al.* (2019) [36]; Wordu and Akusu (2020) [37] revealed the presence of potassium bromate in all the bread products analysed in all the studies. Furthermore, presence of potassium bromate in the entire bread sample analysed was also reported by other studies carried out by Emmanuel and Ernest (2020) [38] in Uyo, Akwa Ibom State and Henrietta (2017) [39] in Asaba, Delta State. Similar findings were obtained by Johnson *et al.* (2013) [23]; Gav *et al.* (2019) [40]; Ekere and Ekere (2020) [41] and Suleiman *et al.* (2020) [18] in their separate studies carried out in Karu of Nasarawa State, Makurdi metropolis of Benue State, Jos Metropolis of Plateau State and Kogi State respectively. Likewise, Magomya *et al.* (2020) [20] reported the presence of potassium bromate in all the 20 bread loaves sampled and analysed in Jalingo metropolis of Taraba State. However, in contrast to our findings Alexander *et al.* (2019) [42] reported the absence of potassium bromate in the entire 10 bread

samples analysed.

Numerous studies showed that potassium bromate reduces the nutritional quality of bread through its ability to degrade important available vitamins in the bread such as vitamins A1, B1, B2, E and niacin (FAO/WHO, 1999) [24]. The findings of our study showed that potassium bromate degrade vitamins A and E as presented in Table 1. Several nutritional studies revealed that potassium bromate degrade vitamins A, B1, B2, E and niacin which are the main vitamins in the bread which conformed to the findings of our study. Furthermore, vitamin A possess a complex chemical structure and contained numerous double bond that are vulnerable to degradation due to factors such as high temperature required for bread baking, excessive light, oxygen and other bread nutritional composition (Uchendu *et al.*, 2012) which may also be another reason for degradation of vitamin A as observed in this study. The factors that can leads to low vitamins content in the bread may be due to low level of vitamin A fortification in the flour because of incompliance of the flour producers to the WHO fortification guideline or poor storage, transportation of the flour products by the producers or bakers to their respective bakeries. Poor transportation and storage of the basic raw materials for bread formulation particularly flour, sugar and oil are what has been reported in most of the bakeries which may leads to the degradation of nutritional content of the raw materials especially vitamins even prior to bread baking process.

The concentration of $KBrO_3$ in Five (5) different major bread improvers used by bread bakers in the State are presented in Table 2. The result of our study showed that all the improvers contained high concentration of potassium bromate. Based on our finding, no research was carried out or documented yet on the determination of potassium bromate content in the bread improver in Nigeria. Most of studies are on the assessment of potassium bromate in the bread products only, with very few that sampled and analysed other bread raw materials. Example Magomya *et al.* (2020)[20] quantify the level of potassium bromate not only in bread but also in flour and the result of his study revealed the presence of potassium bromate in all the bread and flour samples analysed. The finding of our study may expressed the view that most of the bakers do not deliberately add potassium bromate in their bread formulation but been presence in the bread improvers they used. All the bread improvers sampled and analysed are registered by the NAFDAC, hence the reason for the use of these improvers by the bakers. Most of the bakers justified the view that the bakers do not deliberately add potassium bromate in their bread formulation as majority of them are not aware on the content of the improvers, but the only justification available to them is been the improvers registered by NAFDAC. The action of bread improvers as food enhancers may also attribute to its inhibitory action on certain proteolytic enzymes thereby affecting the nutritional quality of bread through degradation of vitamins A, B1, B2, E and niacin as observed in our study.

Likewise, our study quantify the levels of heavy metals such as Nitrite (NO_2^-), Lead (Pb), Cadmium (Cd), Cupper (Cu), Zinc (Zn) and Iron (Fe) in the Fourty (46) bread samples and the result was presented in Table 3. The mean level of nitrite (NO_2^-) ranges from 0.026±0.008mg/kg to 0.397±0.009mg/kg was found in this study which was lower than the range of 0.10 to 4.40mg /kg reported by Nabrzyski *et al.* (1990)[43]. The use of nitrogen fertilizer and sewage sludge on the soil during wheat cultivation which can be converted to Nitrite in the soil and can all be absorbed by wheat root system and accumulated will significantly increase the levels of NO_2^- in the bread (El-Nahhal, 2018) [13]. Similarly, the nitrite deposits in bread samples as observed in this study may be from water used for irrigation of wheat during agricultural processes or from polluted water used for bread processing by various bakeries. Nevertheless the level of the nitrite in the bread sample was found to be apparently low, but it is capable of exposing consumers to high risk by considering the high rate and consistent consumption of bread which can tends to be high level. Consumption of bread containing nitrite may expose the stomach to enormous cancer cells because bread was reported to have at least 6 hours retention time in the stomach for acid digestion and this may leads to release of the nitrite thereby translocating to liver which may subsequently react with genetic memory of cells (RNA/DNA) forming nitrification product (El-Nahhal, 2018) [13].

The findings of our study further revealed that Thirty (30) bread samples analysed contained Lead (Pb) within a range of 0.147±0.095mg/kg to 12.355±0.022mg/kg and out of this only seven (07) samples contained Lead (Pb) within a permissible limit of 0.2 to 2.5mg/kg in a food as recommended by Codex Alimentarius Commission (CAC) (Oyekunle *et al.*, 2014) [15]. In contrast to our findings Irogbeyi *et al.* (2019) [16] reported a range of lead (Pb) in bread to be 0.05±0.01 to 0.45±0.02mg/kg which is lower than some of our results. Likewise, Magomya *et al.* (2013) [2] obtained the concentration of Pb in bread at the range of 0.34mg/kg to 3.03mg/kg. When human body absorbed lead (Pb) it become deposited in some tissues for a long period of time before been released into blood stream and subsequently distributed to the body system (Irogbeyi *et al.*, 2019) [16]. A number of diseases such as cardiovascular, renal, nervous and skeletal system have been associated with excessive content of lead (Pb) in food and the possible source of Pb in the bread may be due to environmental factors such as industrial production processes and their emissions, road traffic with leaded petrol, smoke and dust emissions of coal and gas fired power stations, the laying of Pb sheets by roofers as well as the use of paints and anti-rust agents (Magomya *et al.*, 2013) [2].

However, the result showed that eight (08) bread samples contained Cadmium (Cd) within the range of 0.025±0.006mg/kg to 0.868±0.099mg/kg with four (04) samples out of this number to have the level within the permissible limit of 0.05mg/kg. Study by Magomya *et al.* (2013) [2] reported the level of Cd in the 15 bread samples to be within the range of 0.013mg/kg to 0.098mg/kg which is lower than the range obtained in this study whereas another study by Tejera *et al.* (2013) [44] found the mean contents of Cd in the wheat breads to be 0.027mg/kg which fall within the range of our result. Cadmium is highly toxic element and is considered to be one of the furthermost severe contaminant of modern age. Detrimental health effects such as tubular growth, kidney damage, cancer, diarrhea and incurable vomiting on human have been reported on high concentration of cadmium (Sabine and Wendy, 2009) [45].

Equally, the finding of the study revealed that fourteen (14) bread samples had Cupper (Cu) within the range from 0.001±0.000 mg/kg to 1.684±0.032mg/kg, the level that was

found to be below the permissible limit of 10mg/kg. The study conducted by Irogbeyi *et al.* (2019) [16] reported the levels of Cu in the bread to be in the ranges of 0.31±0.04 to 0.49±0.12 mg/kg. Likewise Oyekunle *et al.* (2014) [15] reported level of Cu in bread within values from 0.23mg/kg to 0.46mg/kg which are also within the range of our result. Another result was reported from Akure metropolis by Tomori and Onibon (2015) [46] where they found the presence of Cu in the cereal based products within the values from 0.03±0.01mg/kg to 2.55±0.25mg/kg which are higher than the level observed in this study.

Equally, twenty (20) samples were observed to contain Zinc (Zn) from the range of 0.009±0.000mg/kg to 1.468±0.021mg/kg which is below the acceptable limit of 50mg/kg. The level Zn in bread found in this study is lower than the level of 0.24-2.11mg/kg, 0.1±0.02 - 3.15±3.15mg/kg and 3.22±0.05 - 7.25±0.24mg/kg reported by Magomya *et al.* (2013) [2] in Zaria; Tomori and Onibon (2015) [46] in Akure and Irogbeyi *et al.* (2019) [16] in Ile-Ife respectively. For adults, an estimated daily intake of Zinc was recommended to be 20mg/day. Deficiency of zinc has been associated with development hindrance, loss of hunger and impeded immune function while its high concentration has been reported to cause severe effects such as vomiting and gastrointestinal irritation leading to nausea, cramps, diarrhea (Magomya *et al.*, 2013; Tomori and Onibon, 2015; Irogbeyi *et al.*, 2019) [2, 46, 16]. The level of zinc in bread observed in our study is below the World Health Organization recommended level in food.

No concentration of Iro (Fe) was detected in any of the bread samples analysed in this study, contrary to the finding of Magomya *et al.* (2013) [2] who reported the level of Fe in the bread samples they analysed to be within 0.62 to 8.45mg/kg.

Several studies attributed the presence of heavy metals in bread to the environment pollution, particularly agricultural soils pollution with heavy metals which are transferred to the root of wheat. Above all some basic raw material required for bread formulation and processing such as contaminated water, salt, sugar, yeast, improvers, preservatives, vegetable oil, and flavours can contaminate the bread with heavy metals (Khaniki *et al.*, 2005) [11]. Similarly, the use of metal equipment instead of inert (e.g stainless steel) in bread processing such as bread baking trays, oven, utensils, moulding machine, mixers may also be the source of heavy metals contamination to the bread. Secondary pollution which may contaminate the bread includes fuels, diesel and lubricants used for the bread processing machineries. Others factors that may contaminate bread with heavy metals include air pollution particularly bakeries situated in urban areas due to high human and industrial activities from both mobile source including cars, buses, planes, trucks and trains, and stationary source such as power plants, oil refineries, industrial facilities and factories.

Conclusion

High concentration of potassium bromate in the bread observed may be attributed to the bread improvers used in the bread formulation as all bread improvers analysed contained potassium bromate. Therefore, findings of this study may express the view that potassium bromate is unintentionally added into the bread but may be deliberately added into bread improvers by their respective manufacturers for economic gain. Concentration of nitrite (NO_2^-), Lead (Pb) and Cadmium (Cd) in the bread sample observed are of great concern to the public health particularly been them highly toxic elements. Cupper (Cu) and Zinc (Zn) are nutritionally essential antioxidants elements, hence they presence in the bread as noticed may help to meet their daily recommended dietary allowance (RDA). Potassium bromate in the bread is of great public health concern, therefore more detection technique need to be employed by the regulatory bodies for on-the-spot analysis of bread. Furthermore, regulatory bodies need to create a means of public sensitization on the hazardous effects of potassium bromate and to also impose stringent regulations for the production and marketing of bread products and its basic ingredients particularly flour, improvers, sugar and others. Most importantly post marketing surveillance of bread and its ingredients by the regulatory bodies are significant to monitor the manufacturers' compliance with all the stipulated production and marketing regulations.

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Conflict of Interest

The authors have declared no conflict of interest. The authors further declared that no other relationships or activities that could appear to have influenced this study.

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