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Assessment of Bread Safety in Gusau- Zamfara State: Qualitative and Quantitative Determination of Potassium Bromate and Some Heavy Metals

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ABSTRACT

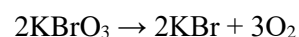
Twenty-six (26) samples of different bread brands sold in Gusau metropolis of Northern Nigeria were analyzed for potassium bromate and some heavy metals content. The study revealed the presence of potassium bromate in all the samples analyzed. The concentrations ranged from 3.45-9.38 mg/kg; all the values were above the allowed limit by FDA of 0.02 µg/g (0.02 mg/kg). Atomic absorption spectroscopic method was used for the heavy metals determination, the heavy metals determined were Pb, Cd, Cu, Zn and Fe, and results obtained were assessed on the basis of the permissible limits for the respective metals in Foods. The concentrations of Pb, and Cd in the samples were in the range of 0.12-1.20 mg/kg and 0.010- 0.081mg/kg respectively. Permissible limit for Pb and Cd in food is 0.2-2.5 mg kg⁻¹ and 0.05 mg/kg respectively. The levels of Cadmium in some of the samples (Samples E, F, H, P R and S) suggest a certain degree of contamination. The values for Cu, Zn and Fe in the samples ranged as follows; Cu (0.03-0.099 mg/kg), Zn (0.24-5.23 mg/kg) and Fe (0.71- 6.67 mg/kg). Cu and Zn content in all the samples were within permissible limits. The concentration for Fe was above permissible limit in one of the samples (samples G, 6.67 mg/kg).

Keywords: Heavy metals, potassium bromate, bread safety, residual potassium bromate and oxidizing agent

1.0 INTRODUCTION

Bread is an important staple food that does not require further processing before consumption (Olusegun *et al.*, 2015). Despite the awareness created and effort of government to ensure high quality bread, there are several routes through which bread is contaminated (Olusegun *et al.*, 2015). Most Bakeries use potassium bromate, a strong oxidizing agent, for bread improving effects such as to preserve flavor or improve the taste and appearance (Adejumo *et al.*, 2016), it also has significant effect on food biomolecules, such as starch and protein, thus improves the bread properties (Shanmugavel *et al.*, 2020). For many years the use Potassium bromate was permitted as a bread conditioner since bromate is converted to bromide, with no traces of it when exposed to heat during bread production (as shown in the equation below) (Kim *et al.*, 2015). However, this is dependent on the quantity of potassium bromate

used and the duration of exposure to optimal temperature (Uwah and Ikwebe 2020).



The un-converted Potassium bromate as a result of high quantity of the additive or limited exposure to optimal temperature will now remain in the baked bread as Residual potassium bromate (RPB), This is why, to assess bread safety: based on potassium bromate content, the major possible means is to assess the RPB from baked bread. The International Agency for Research on Cancer (IARC) classified KBrO₃ as a 2B (a possible human) carcinogen (Sadman *et al* 2021). In addition, Potassium bromate possesses non-cancerous health problems like sore throat, diarrhea, nausea, vomiting and abdominal pain (Adejumo *et al.*, 2016). It is also being reported that continuous consumption of KBrO₃ can cause low blood pressure, depression and thrombocytopenia. (Adejumo *et al.*, 2016).

On account of its deleterious effect and carcinogenicity in humans, the use of potassium bromate in bread processing was banned in many countries including Nigeria. However, despite the ban placed on the use of potassium bromate as bread-enhancer in Nigeria, many researches in other part of the country revealed that baker are still using the additive so as to increase bread volume and texture.

Heavy metals on the other hand, are potential environmental contaminants with the capability of finding their ways into food we eat and causing human problems (Adeosun and Makanjuola 2020). Many chemical compounds and heavy metals are considered as toxic contaminants when they occur in certain levels in food (Rather et al., 2017). The major route for heavy metals exposure in human is mainly through soil-crop-food pathway (Adeosun and Makanjuola 2020). Heavy metals are given special attention throughout the world due to their ubiquitous nature and toxic effects even at very low concentrations (Hassien, 2022). Elements such as Cd, Cr, and Pb are considered carcinogenic while Fe, Cu, Zn, Ni and Mn are considered as essential metals, however, if the concentration of the later elements are higher than their permissible limits, they may create toxic effects in humans (AbdAllah, 2017). However, due to their chemical and physiological properties, many heavy metals are useful in many industrial areas which increase the opportunity for heavy metal exposure.

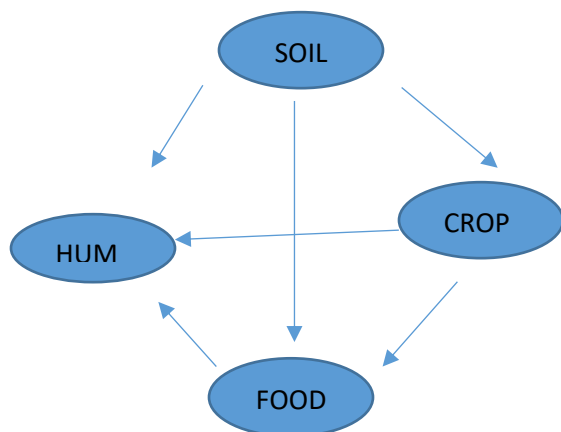


Figure 1 The route for heavy metals exposure in human

The present study determined the content of potassium bromate and some heavy metals in bread samples within Gusau metropolis, Zamfara state, Nigeria

2.0 MATERIALS AND METHODS

2.1 Materials

2.1.1 Collection Samples

Bread samples were purchased/collected from open markets, bus stops and bread vendors within Gusau metropolis. A total of twenty-six (26) different brands of bread were used in the study.

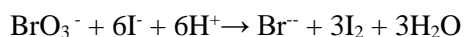
2.1.2 Reagents Used

The following analytical grade reagents were used for the research: hydrochloric acid, promethazine, potassium bromate (BHD Chemicals Ltd, poole, England), concentrated nitric acid, perchloric acid and potassium iodide. Distilled water used was double distilled.

2.2 Methods

2.2.1 Analysis of Potassium Bromate in Bread

Principle; The analyses were based on the fact that Potassium bromate in an acidic medium oxidizes potassium iodide to liberate iodine and producing a purple violet coloration. This is shown in the reaction below:



2.2.2. Qualitative Analysis

The qualitative test was performed using two different methods;

- i. Directly on a portion of each bread sample using promethazine and hydrochloric acid (Alli *et al.*, 2013). Exactly 2 cm³ of 0.01M promethazine and 0.6 cm³ of 12M hydrochloric acid were serially added to a portion of the bread samples and there colour change were observed. The change in colour of the bread samples to pink indicates the presence of potassium bromate.
- ii. Approximately 1.0 g quantity was weighed out from each bread sample and transferred into a test tube. Ten milliliter (10 cm³) of distilled water was added; the mixture was shaken and allowed to stand for about 30 min at 28 ± 10°C.

A 5.0 cm³ volume was decanted from the test tube. A 5.0 cm³ quantity of freshly prepared 0.5% potassium iodide solution in 0.1N hydrochloric acid was added. Color change (pink) was noted (Dagari *et al.*, 2022).

- iii. The presence of potassium bromate was indicated by change in colour from light yellow to purple (Dagari *et al.*, 2022).

2.2.3 Quantitative Determination of Potassium Bromate

2.2.3.1 Calibration Curve

Aliquots of 100 - 1000 μl from the primary stock solution of potassium bromate were placed in 20 cm³ capacity test tubes, and 1 cm³ of 0.01M promethazine (PTZ) was added. Mixtures were then diluted with distilled water up to 10 cm³ to obtain a final concentration of bromate in the range of 0.5 μg/cm³ to 5 μg/cm³, 0.2 cm³ of 12M hydrochloric acid were then added. Mixtures were well shaken for 1-2 minutes and the absorbance was measured at 515nm against a blank reagent, results were used to plot the calibration curve.

2.2.3.2 Preparation of Bread Samples

Exactly 10 g portion was taken from each loaf of bread and dried in an oven at 75°C. The dried crust

was pulverized and 1g of each powdered sample was weighed into a clean 250 cm³ beaker and 20cm³ of distilled water was added. The mixture was stirred thoroughly using a mixer and then filtered using a Whatman no. 1 filter paper. 8.8 cm³ of the filtrate solution was transferred into a 20 cm³ volumetric tube and mixed with 1 cm³ of 0.01M promethazine. 0.2 cm³ of 12M hydrochloric acid was added making a total of 10 cm³. The mixture was shaken for 2 minute and absorbance of the colored solution obtained was measured using a spectrophotometer at 515nm. The concentration was calculated from the linear regression curve obtained from the standard solutions of potassium bromate as mentioned above. Values presented are a mean of three replicate determinations.

2.2.4 Quantitative Determination of Heavy Metals

Exactly 1 g of each of the samples was digested with concentrated nitric acid and perchloric acid in a ratio of 3:1 on a hot plate. It was then filtered using whatman filter No. 1 in to a 50 cm³ volumetric flask and made up to mark with distilled water Metals concentrations were determined using atomic absorption spectrophotometer.

3.0 RESULT AND DISCUSSION

Table 1: Quantitative and qualitative determination of potassium bromate in some brands of bread sold in Gusau, Zamfara State.

S/No.	Bread Samples	Concentration of KBrO ₃ (μg/g)	Colour change (Alli <i>et al.</i> , 2013)	Colour change (Dagari <i>et al.</i> , 2022)
1.	A	9.38 ± 0.31	+++	+++
2.	B	5.61 ± 0.40	++	++
3.	C	6.16 ± 0.22	++	++
4.	D	6.56 ± 0.39	++	+++
5.	E	5.36 ± 0.44	++	++
6.	F	6.24 ± 0.12	++	++
7.	G	7.30 ± 0.47	+++	+++
8.	H	9.30 ± 0.21	+++	+++
9.	I	6.38 ± 0.22	++	++
10.	J	7.38 ± 0.44	+++	+++
11.	K	9.16 ± 0.12	+++	+++
12.	L	3.18 ± 0.22	+	+
13.	M	6.92 ± 0.42	++	+++

14.	N	7.21 ± 0.11	+++	+++
15.	O	8.76 ± 0.22	+++	+++
16.	P	6.72 ± 0.31	++	+++
17.	Q	7.55 ± 0.21	+++	+++
18.	R	3.45 ± 0.34	+	+
19.	S	8.32 ± 0.21	+++	+++
20.	T	6.43 ± 0.33	++	++
21.	U	9.32 ± 0.44	+++	+++
22.	V	4.88 ± 0.20	+	+
23.	W	6.22 ± 0.21	++	++
24.	X	4.21±0.12	+	+
25.	Y	7.13±0.18	+++	+++
26.	Z	6.44±0.13	++	+++

Key; + light yellow ++ yellow +++ dark yellow

Table 2: heavy metal content of some bread samples produced in Gusau, Nigeria (mg/kg)

S/No.	Bread samples	Pb	Cd	Cu	Fe	Zn
1.	A	0.23 ± 0.02	0.012 ± 0.01	0.45±0.04	1.35±0.12	1.25±0.40
2.	B	0.20 ± 0.13	0.021± 0.00	0.09±0.02	2.35±0.20	1.34±0.09
3.	C	0.22 ± 0.01	0.041± 0.00	0.07±0.12	1.03±0.01	0.93±0.02
4.	D	0.91 ± 0.02	0.027± 0.01	0.23±0.01	0.93±0.21	3.76±0.22
5.	E	0.42 ± 0.01	0.061± 0.00	0.37±0.10	3.77±0.23	4.32±0.61
6.	F	0.21 ± 0.10	0.070± 0.01	0.70±0.11	0.89±0.13	1.23±0.23
7.	G	0.20 ± 0.03	0.049± 0.01	0.08±0.03	6.67±0.12	0.24±0.02
8.	H	0.97± 0.23	0.081± 0.02	0.81±0.12	0.92±0.05	2.33±0.12
9.	I	0.12 ± 0.11	0.030± 0.01	0.99±0.08	1.56±0.21	3.12±0.21
10.	J	0.21 ± 0.21	0.020± 0.01	0.23±0.23	1.23±0.13	0.78±0.05
11.	K	0.22 ± 0.11	0.013± 0.02	0.34±0.11	3.77±0.11	3.34±0.02
12.	L	0.20 ± 0.00	0.029± 0.01	0.23±0.23	1.76±0.31	5.23±0.21
13.	M	0.90 ± 0.21	0.010± 0.01	0.21±0.11	4.22±0.03	0.98±0.10
14.	N	0.32 ± 0.41	0.020± 0.00	0.67±0.22	0.71±0.01	2.34±0.52
15.	O	0.21 ± 0.11	0.042± 0.01	0.37±0.02	2.56±0.33	1.09±0.21
16.	P	1.20 ± 0.01	0.057± 0.01	0.32±0.09	1.68±0.02	2.98±0.27
17.	Q	0.28 ± 0.11	0.035± 0.02	0.65±0.02	3.27±0.01	1.23±0.21
18.	R	0.91 ± 0.22	0.076± 0.01	0.07±0.05	0.88±0.03	3.22±0.03
19.	S	0.90 ± 0.34	0.063± 0.01	0.21±0.11	1.98±0.12	1.45±0.28
20.	T	0.20 ± 0.00	0.033± 0.01	0.32±0.01	0.89±0.21	0.98±0.04
21.	U	0.28 ± 0.11	0.032± 0.02	0.26±0.20	3.73±0.02	0.89±0.02
22.	V	0.20 ± 0.22	0.029± 0.00	0.32±0.02	1.56±0.33	1.78±0.22
23.	W	0.98 ± 0.02	0.032± 0.01	0.07±0.10	1.25±0.78	3.24±0.05
24.	X	0.27 ± 0.13	0.014± 0.02	0.11±0.03	1.45±0.09	1.78±0.20
25.	Y	0.37 ± 0.54	0.026± 0.01	0.42±0.10	2.56±0.21	2.45±0.25
26.	Z	0.22 ± 0.01	0.041± 0.02	0.03±0.01	4.34±0.35	1.72±0.54

3.2 DISCUSSION

The maximum allowable bromate concentration in bread by FDA is 0.02 mg kg⁻¹ (Shanmugavel et al., 2020). All the samples analyzed in the present

study had potassium bromate in excess of the allowed concentration. Similar research conducted on bread samples obtained from different parts of the country by Magomya et al, Ekere et al,

Airaodion et al., Ranged from 1.16 -10.44 mg/kg, 3.70 - 12.10 mg/kg, 2.46-13.60mg/kg, 0.25-4.375 mg/g), 1.24-9.31mg/kg respectively. However, Naze *et al.*, has reported one out of the thirty bread samples analyzed in Port Harcourt Metropolis, Rivers State contain potassium bromate within the permissible limit (0.011mg/kg). The mean concentration of potassium bromate in all the samples was significantly different ($p < 0.05$) from the maximum permissible level of 0.02 mg/Kg established by the United State Food and Drug Administration (US. FDA) for potassium bromated in bread

This simply means that, none of the bread samples analyzed in this study is safe for human consumption as far as potassium bromate content is concerned as the sample with the smallest concentration of KBrO_3 contains 3.18 $\mu\text{g/g}$ (which is more than 150 times higher than the permissible safe level).

The presence of such high levels of potassium bromate in bread is highly undesirable considering its deleterious effects. Toxicological studies have also convincingly shown that potassium bromate affects the nutritional quality of bread by degrading the main vitamins available (Shanmugavel *et al.* 2020).

Table 2 shows the concentrations of Pb, Cd, Cu, Fe and Zn in the bread samples analyzed.

In 2010, a high number of child fatalities was reported in Zamfara state (MSF 2012), which is confirm to be as a result of high level of lead in the blood samples of the surviving children. The root cause of the lead poisoning was attributed to unsafe mining and ore processing in the area, although morbidity-prevalence in the state has effectively reduced from >97% (in 2010) to <3% (in 2018), there are still >3000 under five years who are still exposed to Lead poisoning as a result of ineffective re-contamination control among other reasons (MSF,2012). However, the result obtained shows that the concentration of Pb observed in all the samples analyzed (0.12-1.20mg/kg) are within the permissible limit. Permissible level of Lead in food is in the range of 0.2-2.5 mg kg⁻¹.

The level of Cd in the bread samples analyzed ranged from 0.010- 0.081mg/kg. Permissible limit for Cd in food is 0.05mg/kg (Genchi, et al., 2020). From the results obtained, six (6) out of the twenty-six (26) samples analyzed had Cd concentration above the permissible limit. Sample H has the highest level of Cd which is about 1.62 times higher than the permissible limit. These results are of concern as cadmium is highly toxic, non-essential transition metal and high concentration of cadmium exerts detrimental effects on health of both humans and animals (Genchi, et al., 2020), some of the effect caused by high concentration of Cd include severe diseases like tubular growth, kidney damage, cancer, diarrhea and incurable vomiting (Adejumo *et al.*, 2016).

Some heavy metals, such as Cu, Zn and Fe are nutritionally essential metals (Magomya *et al.*, 2013), copper (Cu) and zinc (Zn), serve as enzymes that are essential for intracellular processes and have DNA-binding domains (Magonya et al 2013). However, these metals are toxic when taken in excess (Magonya et al 2013) and is associated with a number of diseases, especially of the cardiovascular, renal, nervous and skeletal systems. The concentration of Cu in the bread samples ranged from 0.03-0.99 mg/kg. These concentrations are far below the permissible level of Cu in foods (Asif, Sharf and Anwar 2020). The samples can therefore be considered free from Cu contamination.

The average daily intake of zinc has been estimated to be maximally 20 mg/day for adults (Magonya et al 2013). In human, high levels of zinc have been associated with acute effects such as vomiting and gastrointestinal irritation. The highest Zn concentration in the bread samples analyzed was observed for sample L (5.23mg/kg) while the lowest was in sample G (0.24mg/kg). These values are within the permissible level of Zn in foods (Asif, Sharf and Anwar 2020).

Iron is an essential element for almost all living organisms as it participates in a wide variety of metabolic processes, including oxygen transport, deoxyribonucleic acid (DNA) synthesis, and electron transport (Abbaspour, et al 2013). it is required for the synthesis of haemoglobin: a protein

in red blood cells that carries oxygen from the lungs to all parts of the body, and in many enzyme systems (Harvard T.H SPH 2022). Iron is also part of myoglobin, a protein that carries and stores oxygen specifically in muscle tissues. Iron is important for healthy brain development and growth in children, and for the normal production and function of various cells and hormones (Harvard T.H SPH 2022) Various groups differ in requirement for iron: the recommended dietary allowance (RDA) for adults (19-50 years) is 8 mg/day for men, 18 mg/day for women, 27 mg/day for pregnancy and 9 mg for lactation (IMFNB,2001). However, it can lead to tissue damage when in excess (Abbaspour, et al 2013).

The concentrations of Fe in the bread samples studied ranged from 0.71-6.67 mg kg¹. The permissible limit for Fe in food is in the range of 2.5-5.0 mg/kg depending on the foodstuff. Samples G had iron concentrations above the permissible level (6.67 mg/kg). However, in human, acute toxicity of iron ingested from normal dietary sources has not been reported (Magomya et al., 2013). Toxicity is rare because the body regulates iron absorption and will absorb less if iron stores are adequate (Harvard T. H Chan, 2022).

Metal containers used for kneading of dough during bread making may be responsible for high levels of such metals. Environmental contamination such as Atmospheric deposition from urban and industrial areas may result in contamination of agricultural produce with heavy metals which are in turn transferred to the finished products.

4.0. CONCLUSION

This research has provided valuable information about the potassium bromate and heavy metal contents of bread brands produced in Gusau, Zamfara state, Nigeria. All the twenty- six bread samples investigated contained potassium bromate

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in quantities that exceeded the allowed limits by FDA. These findings simply imply that Bakers in Gusau, Nigeria still use potassium bromate for bread making despite its ban in 1993 by the Nigerian National Agency for Food, Drug Administration and Control (NAFDAC). This call for a proactive measure from policymakers and regulatory agencies against the use of potassium bromate as an additive in bread production. It is equally important to sensitize bakers on the health hazard of potassium bromate to consumers and their employees and to enlighten them about non-toxic alternatives such as ascorbic acid (Vitamin C), potassium iodate (KIO₃) and azodicarbonamide. alongside a suitable enzyme (Asif, Sharf and Anwar 2020).

Results of the heavy metal analysis showed that the levels of Cu and Zn are generally within safe limits. However, the concentrations of Fe and Cd in some of the samples were above permissible levels. All the samples analyzed contained some level of lead. Therefore, there is need for relevant agencies to carry out regular monitoring of bakeries to ensure that the bakers do not flout the laws and that the environment and indeed the materials used by these bakeries are devoid of contamination of any kind so as to safeguard the health of the consumers.

5.0 RECOMMENDATIONS

- i. We recommend a robust nationwide study on the compliance of the baking industry to the use of potassium bromate.
- ii. Government should provide the alternative conditioners at a subsidized rate to the production industries

6.0 ACKNOWLEDGEMENT

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