COMPARATIVE LEVELS OF BROMATE AND METALS IN BREAD LOAVES OBTAINED FROM CORPORATE AND LOCAL BAKERIES IN TWO COMMUNITIES OF LAGOS, NIGERIA

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Abstract: A comparative assessment of potassium bromate and trace/toxic metal levels in bread loaves obtained from selected corporate and local bakeries in two communities of Lagos, Nigeria, was carried out using High Performance Liquid Chromatography (HPLC) and Atomic Absorption Spectrophotometry (AAS). Potassium bromate was present in bread loaves obtained from both corporate and local bakeries, but the bread loaves obtained from local bakeries had significantly higher (p < 0.05) bromate levels. The lowest bromate levels in bread loaves obtained from corporate bakeries was 1.18 ± 0.01 mg/kg, while the highest was 2.26 ± 0.01 mg/kg. The lowest and highest bromate levels in bread loaves obtained from local bakeries were 3.85 ± 0.01 and 11.13 ± 0.00 mg/kg, respectively. The concentrations of metals in the sampled bread loaves were generally below regulatory limits. Bread loaves obtained from corporate bakery 5 had the highest Zn content of 3.26 ± 0.06 mg/kg bread, while the lowest Zn level in finished products (0.02 mg/kg) on bromate levels in bread loaves obtained from local bakeries and other wheat flour food products (Nakamura et al., 2006; Emeje et al., 2014). High Performance Liquid Chromatography (HPLC) is a suitable method for detecting bromate at extremely low concentration levels without extensive sample treatment (Kujore and Serret, 2010). Unlike bromate, metals are not bread additives; but they may get into bread from the wheat flour used in bread production, or from some other sources during production like the water and salt added to flour, the fuel used for baking, contact with metal surface during mixing and kneading dough, packaging materials etc. (Ahmed and Fadel, 2012; Magomya et al., 2013). Above certain concentrations, metals, some of which are classified as essential elements, are toxic to humans causing various diseases. Depending on the type of metal, the health effects of metal poisoning include gastrointestinal disorders, tremor, diarhhea, paralysis, vomiting, convulsion, diabetes, cancer, anaemia, encelopathy etc. (Durulibeet et al., 2007; Adefris, 2011). Heavy metals disrupt the physiological functions of the body by accumulating in vital organs and glands such as the heart, brain, kidney, bone, and liver (Ray and Ray, 2009).

Keywords: ‘Agege bread’, bakers, potassium bromate, staple food

Introduction
In many countries including Nigeria, bread is a staple food that is eaten daily in many homes. A lot of standard corporate bakeries are spread all over the city of Lagos but these seem too few to meet the high bread demand occasioned by the city’s high population density. This situation has given room for local and substandard bakeries to thrive. While the corporate bakeries may be open to regulatory inspections, the same may not be said of most of the local bakeries. The operations of these local bakeries are discreet, and it is doubtful if they can be under the proper watch of any regulatory body. They operate under unhygienic conditions and the bread loaves they push out are usually unbranded or unlabelled. The implication of this is that it is not easy to trace any particular loaf of bread to a baker or address even when contamination or unwholesomeness is suspected in such a loaf. The operators of these bakeries ride on the ignorance of their customers, majority of whom are uninformed, to make brisk business. The bread loaves that come out of these local bakeries are so popular in Lagos that they are fondly referred to in local parlance as ‘Agege bread’.

Some bread loaves are known to contain additives and contaminants that are deleterious to human health. Two of such contaminants are potassium bromate and metals (Kurokawa et al., 1990). Potassium bromate (KBrO₃) is a colourless, odourless and tasteless white crystal or powder that is used as a flour improver (conditioning agent). It is a maturing agent that acts principally in the late dough stage giving strength to the dough during the late proofing and early baking (Kurokawa et al., 1990). Bromate makes bread rise in the oven and increases loaf volume and texture, thereby making the finished loaves appealing to the public. It does this by oxidizing the sulphhydryl groups of the gluten protein in flour to disulphide bridges, making it less extensible and more elastic such that it can retain carbon dioxide gas produced by the yeast (Emeje et al., 2010: Ojo et al., 2013). Upon the discovery that bromate is toxic and carcinogenic in man, having the capacity to cause diseases such as cancer and kidney failure, the Food and Agricultural Organization (FAO) and World Health Organization (WHO) joint action committee prohibited the use of bromate as a bread quality improver (FAO/WHO, 1999). In California, the American Bakers Association (ABA) and American Institute of Baking International (AIBI) adopted a limit of 0.02 mg/kg on bromate level in finished products (ABA/AIBI, 2008). In Nigeria, the use of bromate in flour milling and baking was banned in 2003 (Oyekunle et al., 2014), but in spite this ban, assessment studies have consistently found high levels of bromate in bread and other wheat flour food products (Nakamura et al., 2006; Emeje et al., 2010; Magomya et al., 2013; Oyekunle et al., 2014). High Performance Liquid Chromatography (HPLC) is a suitable method for detecting bromate at extremely low concentration levels without extensive sample preparation (Kujore and Serret, 2010). Unlike bromate, metals are not bread additives; but they may get into bread from the wheat flour used in bread production, or from some other sources during production like the water and salt added to flour, the fuel used for baking, contact with metal surface during mixing and kneading dough, packaging materials etc. (Ahmed and Fadel, 2012; Magomya et al., 2013). Above certain concentrations, metals, some of which are classified as essential elements, are toxic to humans causing various diseases. Depending on the type of metal, the health effects of metal poisoning include gastrointestinal disorders, tremor, diarhhea, paralysis, vomiting, convulsion, diabetes, cancer, anaemia, encelopathy etc. (Durulibeet et al., 2007; Adefris, 2011). Heavy metals disrupt the physiological functions of the body by accumulating in vital organs and glands such as the heart, brain, kidney, bone, and liver (Ray and Ray, 2009).
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Materials and Methods

**Description of study area and sampling**

Ten bakeries were visited in Yaba and Bariga areas of Lagos, Nigeria. Yaba is located on Latitude 6.5084 and Longitude 3.3842. Bariga is located on Latitude 3.3947 and Longitude 6.535. The bakeries visited were made up of five corporate bakeries and five local bakeries. A loaf of bread was obtained from each bakery for three consecutive days. In all, 30 loaves of bread were sampled for the study.

**Digestion of bread samples for bromate analysis**

Bread samples were digested prior to potassium bromate analysis. Each bread sample was left open overnight and thereafter homogenized using an electric blender. Of the homogenized sample, 20.00 g was put into a beaker and 20 ml of acetonitrile was added into it. The mixture was stirred continuously for 15 min and was allowed to stand for 20 min. Thereafter, the mixture was filtered into a 25 ml standard flask and made up to the mark with acetonitrile.

**Analysis of bromate in digested bread samples**

To determine potassium bromate concentrations in digested bread samples, 5 ml of standard form of potassium bromate was first prepared and introduced into the HPLC machine to generate a chromatogram with a Peak Area and Concentration. The standard Peak Area generated was 13054.0298, while the Concentration of the standard was 39.09 mg/kg. This was used to standardize the HPLC before injecting 5 ml of the test sample. A corresponding Peak Area and Concentration chromatogram was also generated for the test sample. The peak Area of the test sample was then compared to the Peak Area of the standard relative to the Concentration of the standard to get the concentration of the sample using the equation:

\[
\text{Concentration of sample (mg per kg)} = \frac{\text{Peak Area of sample} \times \text{Concentration of standard}}{\text{Peak Area of standard}}
\]

**Determination of metals in bread samples**

To determine the levels of metals in bread samples, each bread sample was left open overnight and consequently homogenized using an electric blender. Of the homogenized sample, 20.00 g was weighed into a conical flask. Dilute HNO\(_3\) (HNO\(_3\) : deionized water = 1:3) was added to the sample in a conical flask and was heated in a Bunsen burner until all the reddish yellow fumes were expelled. The solution was brought down, allowed to cool, and was filtered through No. 1 Whatman filter paper into a 10 ml standard flask. The standard flask was made up to mark with deionized water, ready for analysis of metal contents using Atomic Absorption Spectrometer (AAS) (Perkin Elmer model 460).

**Analysis of metals in digested samples**

A suitable standard curve was generated in the AAS using standard solutions of the desired metals. Standard concentrations of 6, 12, 18, 24, 30 mg/kg were used. Adequate standard was generated for each metal passing through the origin. After a good curve was achieved, the digested sample solutions were aspirated into the AAS for the analysis. A unique cathode lamp for each metal was utilized for the analysis, operating at its peculiar maximum operational wavelength. A digital concentration read-out (meter) gave the direct concentration of the metals as contained in the test samples.

**Statistical analyses of data**

The data obtained were analyzed by one-way analysis of variance (ANOVA). Mean differences were compared using the Least Significant Difference (LSD) test. Results obtained from bromate analysis were individually compared with the standards (permissible levels) using One-sample T-test. The bromate and metal levels for corporate bakery bread loaves and local bakery (‘Agege’) bread loaves were compared using the Independent samples T-test. All statistical analyses were done using the SPSS (version 20).

**Results and Discussion**

**Potassium bromate levels in bread loaves obtained from corporate and local bakeries**

Results revealed that bread loaves obtained from both corporate and local bakeries contained significantly higher (p < 0.05) bromate levels relative to the 0.02 mg/kg permissible level set by California ABA/AIBI (2008), and the zero level set by FAO/WHO (1999) and National Agency for Food and Drug Administration and Control (NAFDAC) of Nigeria. The Independent Samples T-test revealed that bread loaves obtained from local bakeries had significantly higher (p < 0.05) bromate levels compared with the ones obtained from corporate bakeries. The mean bromate levels in bread loaves obtained from corporate bakeries 1 to 5 were 1.34 ± 0.00, 1.65 ± 0.00, 2.26 ± 0.01, 1.26 ± 0.01 and 1.18 ± 0.01 mg/kg, respectively. On the other hand, the mean bromate levels in loaves obtained from local (‘Agege’) bakeries 1 to 5 stood at 10.57 ± 0.01, 11.13 ± 0.00, 9.62 ± 0.01, 3.85 ± 0.01 and 7.87 ± 0.00 mg/kg, respectively (Fig. 1).

In agreement with several previous studies (Nakamura et al., 2006; Emeje et al., 2010; Magomya et al., 2013; Oyekunle et al., 2014), the occurrence of potassium bromate at different concentrations in bread loaves sampled for this study reaffirms the disregard for regulatory warnings against bromate use in Nigeria. Though previous studies were not categorical about the types or categories of bakeries the bread they worked on were sourced, the bromate contents in bread loaves sampled in this study compared favourably well with those of some previous studies (Emeje et al., 2010; Magomya et al., 2013), but were surpassed by bromate levels found by Oyekunle et al. (2014). The continued rolling out of bromated bread in Nigeria is an indictment of regulatory agencies in the country. The potential health effects of persistent consumption of bromated bread cannot be overemphasized in view of the fact that bromate has been linked to some health conditions like cancer, kidney failure, abdominal pain, hypotension and deafness in experimental animals and humans (Campbell, 2006; Chipmanet al., 2006; Ojo et al., 2013). More worrisome is the fact that the health effects of bromate toxicity may not be immediate; and when the effects finally manifest, they may not be easily traceable to the root cause, bromated bread consumption.

![Fig. 1: Potassium bromate levels in bread loaves obtained from corporate and local bakeries](image-url)
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standards in so many ways. They operate in sub-standard buildings, sometimes within residential buildings. Most times, there are no visible official sign or signboard to indicate their presence in places where they operate. It is not uncommon to see ‘mobile’ bakers queue up to use one bakery-house on lease. All these are indications of underground operations, and regulation avoidance. One major reason why some bakers have continued to use bromate for baking is to maximise profit. Bromate makes bread to rise in the oven. It increases loaf volume and texture, thereby making the finished loaves appealing to the public. It does these by oxidizing the sulphhydryl groups of the gluten protein in flour to disulphide bridges, making it less extensible and more elastic such that it can retain carbon dioxide gas produced by the yeast (Emejetal., 2010; Ojo et al., 2013). However, there are safe and harmless flour improvers that can be used in place of bromate; these include ascorbic acid and azodicarbonamide (Emejetal., 2014). Government should formulate policies that will make these alternative flour improvers easily affordable and obtainable. This will likely draw the attention of bakers away from bromate. A little understanding of the chemistry of action of potassium bromate may help reduce one’s exposure to its toxicity. If baking is carried out under a considerably high oven temperature with adequate heat exposure time, potassium bromate (KBrO₃) tends to get reduced to potassium bromide (KBr), which is considered harmless (Kujore and Serret, 2010). Therefore when in doubt over the bromate status of bread loaves, a preference for visibly well-baked, brown loaves over less brown, creamy white loaves will likely be a safe decision to reduce exposure to bromate toxicity.

**Metal levels in bread loaves obtained from corporate and local bakeries**

Results of trace/toxic metal analyses indicated that all the sampled bread loaves contained traces of metals (Table 1). Bread loaves obtained from corporate bakery 5 had the highest Zn content of 3.26 ± 0.06 mg/kg bread, while the lowest Zn level of 1.18 ± 0.03 mg/kg was found in loaves obtained from local bakery 2. Bread loaves obtained from local bakeries 1, 2, and 3 had Pb contents of 1.26 ± 0.01, 1.26 ± 0.02 and 0.59 ± 0.02 mg/kg, respectively. Bread loaves obtained from corporate bakery 1 had a mean Co content of 0.01 ± 0.01 mg/kg while loaves obtained from local bakeries 3 and 4 had Co contents of 0.08 ± 0.01 and 0.06 ± 0.00 mg/kg, respectively. Mean Cd levels of 0.10 ± 0.00 and 0.02 ± 0.00 mg/kg were found in bread loaves obtained from local bakeries 1 and 3, respectively, while the metal (Cd) was not detected in loaves obtained from corporate bakeries. The differences in mean concentrations of each the metals (Zn, Pb, Cd, Co) in bread loaves obtained from all the bakeries were not significant (P > 0.05).

**Table 1: Metal levels in bread loaves obtained from corporate and local bakeries**

<table>
<thead>
<tr>
<th>Metals (mg/kg)</th>
<th>Source of bread loaves</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Corporate bakery 1</td>
</tr>
<tr>
<td>Zn mean ± SD</td>
<td>3.12 ± 0.02</td>
</tr>
<tr>
<td>WHO Limit</td>
<td>5.00 mg/kg</td>
</tr>
<tr>
<td>Zn mean+SD</td>
<td>0.01 ± 0.00</td>
</tr>
<tr>
<td>Pb mean+SD</td>
<td>0.01 ± 0.01</td>
</tr>
<tr>
<td>Pb WHO Limit</td>
<td>0.01 mg/kg</td>
</tr>
<tr>
<td>Co mean±SD</td>
<td>0.10 ± 0.00</td>
</tr>
<tr>
<td>Co WHO Limit</td>
<td>0.02 mg/kg</td>
</tr>
<tr>
<td>Cd mean±SD</td>
<td>ND</td>
</tr>
<tr>
<td>Cd WHO Limit</td>
<td>0.01 mg/kg</td>
</tr>
</tbody>
</table>

ND = Not detected. Differences in mean concentrations of each the metals (Zn, Pb, Cd, Co) in bread loaves from all the bakeries not significant (P > 0.05). Values are means of triplicate analyses.

Bread may get contaminated by metals from the wheat flour used in baking, or from some other sources during production (Ahmed and Fadel, 2012; Magomyaat et al., 2013). Though metals were detected only in traces and below the limits set by WHO, this should not be taken for granted considering the fact bread is a staple food that is eaten daily by many people in Nigeria. In addition, individuals are often exposed to more than one metal from more than one source. Therefore, consistent and long-term accumulation of these metals may result in toxicity. Depending on the type of metals, the health effects of metal toxicity may include gastrointestinal disorders, tremor, diarrhoea, paralysis, vomiting, convulsion, diabetes, cancer, anaemia, encopretal, etc. (Duruibe et al., 2007; Adefris, 2011). Heavy metals disrupt the physiological functions of the body by accumulating in vital organs and glands such as the heart, brain, kidney, bone, and liver (Ray and Ray, 2009).

It is recommended that regulatory agencies should take adequate steps aimed at ensuring safety compliance among bakers generally, and sub-standard local ones especially. Moreover, governments at different levels should embark on mass enlightenment campaign to sensitize the citizenry to the dangers inherent in production and consumption of bromated foods. Appropriate policies should be put in place to ensure a minimum standard for bakery business. Bakery business should be restricted to the licensed and the certificated, and should not be an all-comers affair. Wheat flour manufacturers should avoid practices that may raise metal levels in the final products they sell to bakers.

**Conclusion**

Results from this study indicated that bread bakers in Lagos, Nigeria, engage in the use of potassium bromate to improve bread quality. It is therefore evident that some bakers in Lagos have refused to obey the restriction order placed on the use of...
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bromate as a bread quality improver. Regulatory authorities are called upon to check the excesses of bread bakers, especially those who operate substandard bakeries and roll out unlabelled loaves popularly referred to in Lagos as ‘Agege bread’.

References