

## Bromate Residues in Some Popular Baked Products in Relation to the Sustained Antibromate Campaign in Nigeria

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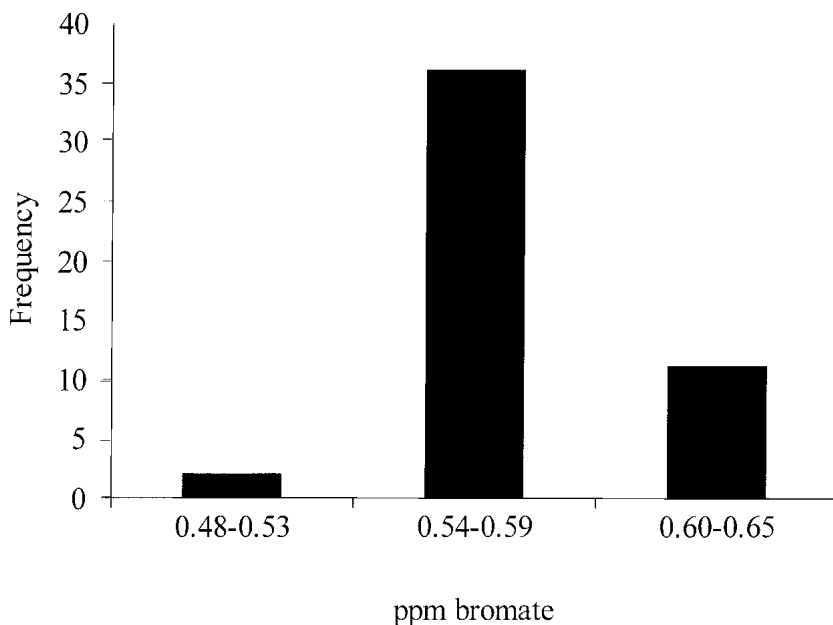
Potassium bromate is an oxidizing agent used in the confectionery industry as a maturing agent for flour and as a dough improver [IARC, 1986; Mack, 1988; Chipman *et al.*, 1998]. However the use of this food additive has been outlawed in many countries on the basis of its well-established harmful effects [CSIP, 1999]. Several mutagenic and carcinogenic effects of bromate have been reported in experimental animals [Ishidate *et al.*, 1984; Umemura *et al.*, 1998; Kurokawa *et al.*, 1987; Chipman *et al.*, 1998; Giri *et al.*, 1999]. Indeed bromate is a well-known kidney carcinogen [Watanabe *et al.*, 2001]. Recently the potential role of bromate-induced oxidative stress in impairment of ocular function was reported [Okolie and Ikewuchi, 2004]. Earlier-on, analysis of some bread samples sold in some metropolitan cities in Nigeria revealed the presence of high levels of residual bromate [Okolie and Osarenren, 2003]. The National Agency for Food, Drug and Administration Control, NAFDAC, a Nigerian government parastatal is the arrowhead of an on-going intensive campaign against the use of bromate by Nigerian bakers. Following this campaign, many brands of bread now bear bromate-free labels. In order to ascertain the veracity of these bromate-free claims and establish the degree of continuing compliance with NAFDAC directives, this investigation is focused on screening of representative samples of popular brands of bread and biscuit in Nigeria for bromate levels. It is posited here that continuous screening of dough-based products for bromate is imperative in a country like Nigeria where relapses into non-compliance are a real possibility. The samples covered in the present studies have not been screened in the earlier studies.

### MATERIALS AND METHODS

49 samples of popular brands of baked products, made up of 44 bread and 5 biscuit products were purchased from retail outlets in 12 major cities in Nigeria. In addition a sample of unprocessed flour from a well-patronised flour mill was obtained from a local distributor shop in Benin City. The bread, biscuit and flour samples were analysed for bromate levels according to the titrimetric method of the Association of Official Analytical Chemists (AOAC, 1980). 50g of each sample was evenly dispersed (in 2g portions) by stirring in 200mL of 0.1M ZnSO<sub>4</sub> solution in a 500mL beaker. Then 50mL of 0.4M NaOH was added and the suspension was stirred for 5min before it was filtered through a Whatman No 12 filter paper. To 50mL of the filtrate in a 250mL Erlenmeyer flask were added, in sequence, 10mL of 4M H<sub>2</sub>SO<sub>4</sub>, 1mL of 1.88M K<sub>1</sub>, 1 drop of 3% (w/v) ammonium molybdate and 50mL of deionized water. As the mixture was being stirred, 10mL of 0.00359M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> was added, followed by

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5mL of 1% (w/v) starch solution. The excess  $\text{Na}_2\text{S}_2\text{O}_3$  was subsequently back- titrated against 0.00359M  $\text{KIO}_3$  to yield a faint purple hue. The titre was noted and the titration was continued after further addition of 1mL of  $\text{Na}_2\text{S}_2\text{O}_3$ . At the end-point the mean difference between the volume in mL of  $\text{Na}_2\text{S}_2\text{O}_3$  added and the volume in mL of  $\text{KIO}_3$  consumed in the 2 titrations was deduced and converted to ppm bromate by multiplying with a factor of 10 [AOAC, 1980]. The resultant values were corrected by using a recovery factor, obtained in a repeat titration using an extract of a non-brominated product (corn flour) containing a known amount of  $\text{KBrO}_3$ . The “recovered” bromate was then compared with “added” bromate. The value of the added bromate was obtained by titrating directly, an equivalent amount of bromate used in “recovery.”



**Figure 1:** Frequency distribution of bromate in the samples

## RESULTS AND DISCUSSION

Table 1 shows the results obtained in the comparison of “added” and “recovered” bromate. A recovery factor of 1.006 was recorded. This is consistent with the value of recovery factor obtained in a previous report [Okolie and Osarenren, 2003], and it clearly shows that the iodometric titration procedure is sensitive and reproducible.

Fig 1 depicts the bromate levels in the baked products analysed. Values were in the range 0.53 – 0.63 ppm. 36 samples (73%) had bromate residues within the range of 0.54 – 0.59 ppm, while 11 (27%) were in the range 0.60 – 0.65 ppm. The mean bromate concentrations in samples obtained from the cities covered are shown in Table 2. The highest bromate levels were recorded in products from Owerri, while Kaduna samples had the least. The sample size used in a given city was a reflection of the

diversity of bakery products in that location. For example Lagos, the highly industrialized and densely populated commercial capital of Nigeria apparently has more brands of bread than any other city in the country. The levels of residual bromate in the bread and biscuit samples analysed [0.53 – 0.63 ppm] were much lower than those reported recently [1 – 16ppm] for similar products in Nigeria [Okolie and Osarenren, 2003]. This indicates a considerable degree of compliance with acceptable bakery practices as they concern bromate use. However, it is clear that the bromate-free labels advertised on many Nigerian brands of bread is questionable. Analysis of the flour sample from a well-patronised flour milling firm indicated a bromate level of 0.58ppm. Bromate is used to mature flour during milling [IARC, 1986]. Thus it is possible that some of the bromate detected in some of the bakery products investigated in the present studies might have emanated from the flour.

However it is known that most of the bromate added to flour during the maturing process is broken down to bromide at the baking stage [IARC, 1986]. This implies that bromate levels in dough decline after baking. Since the bromate content of the unprocessed flour approximated the bromate levels of some of the baked products, the presence of exogenously added bromate is indicated. In addition the closeness of residual bromate values of flour (from the major flour miller) and the baked products could mean that as a consequence of the sustained anti-bromate campaign by NAFDAC, the production methods employed by the various bakers have become essentially the same and obviously standardized (Nigerian Bakers meet regularly under the aegis of Master Bakers Association). Accordingly, residual bromate levels of products become similar due to common route of disintegration or possibly as a result

**Table 1:** Comparison of “added” bromate and “recovered” bromate

Sample	Bromate level (ppm)
Corn Flour	0
Corn Flour + $\text{KBrO}_3$ (recovered bromate)	6
$\text{KBrO}_3$ (added bromate)	6.0365
Recovery Factor (added bromate/recovered bromate)	1.006

**Table 2:** Mean bromate levels of baked products in the locations studied

Sample/Location	Bromate (ppm)	Number of Samples
Lagos	$0.571 \pm 0.017$	15
Benin	$0.573 \pm 0.012$	11
Warri	$0.60 \pm 0.013$	8
Kaduna	$0.559 \pm 0.019$	7
Kano	$0.594 \pm 0.004$	4
Owerri	$0.601 \pm 0.018$	4

Values are Mean  $\pm$  SEM

of similarity in the amount of bromate used. It is also possible that most of the Nigerian bakeries source their flour from this dominant flour miller, going by its long history of operation and the enormous volume of products it churns out regularly into the Nigerian flour market.

Due to the harmful effects of bromate such as carcinogenicity in experimental animals, the Joint Expert Committee on Food Additives, JECFA, has recommended that there should be no bromate residues when  $\text{KBrO}_3$  is employed in food processing [JECFA, 1989]. Cogswell [1997] has suggested ways of achieving non-detectable levels of bromate in baked products. These include, amongst others, the use of lower levels of added bromate ( $< 30\text{ppm}$ ), use of ascorbic acid, longer fermentation and baking times as well as low dough pH. The lethal oral doses of bromate in man are  $154 - 385 \text{ mg/kg}$  body weight, while doses of  $46 - 92\text{mg/kg}$  body weight have resulted in serious poisoning [Mack, 1988]. Bromate doses of  $185 - 385 \text{ mg/kg}$  body weight result in some permanent lesions such as renal failure and deafness, while at lower doses, reversible symptoms such as abdominal pain, diarrhoea, nausea, vomiting, pulmonary oedema, seizures and respiratory depression result [Mack, 1988]. Although the bromate levels of the baked products investigated in this study are much lower than those reported previously [Okolie and Osarenren], they are nevertheless much higher than the accepted provisional guideline value of  $0.025\text{ppm}$  as recommended by the World Health Organisation, WHO [WHO, 1996]. Thus, it appears that Nigerian baked products still contain potentially hazardous residual bromate.

This study has demonstrated that Nigerian bakers still use  $\text{KBrO}_3$ , although at much lower levels than hitherto reported. There is need for more aggressive anti-bromate enforcement campaigns in Nigeria. The detection of toxic levels of bromate in unprocessed flour also necessitates the extension of these campaigns to flour millers.

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