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Analysis of Potassium Bromate Contents of Commonly Consumed Loaves of Bread Samples in Tokra-Libya

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ABSTRACT

Bread is one of the most popular foods consumed worldwide. It is a very popular foodstuff consumed in almost every house in Libya as well as in Tokra city as breakfast. Potassium bromate is an oxidizing agent that has been used as bread additive added to preserve the flavour and teste of the bread but continuing to consume it endangers health as a result of its carcinogenic effect, as it remains in the loaf of bread without disintegration, For this reason, Potassium bromate is banned in several countries, including Brazil, Canada, the European Union and the United Kingdom and the FDA has since 1991 merely encouraged bakers to voluntarily stop using it, with somewhat limited success. In this study, levels of residual bromate were determined in 21commercial breads and traditional loaf types from 7 automated bakeries, except for one, a manual bakery randomly were collected from different local bakeries in Tokra city and its environs (Libya), in Feb. 2023. The tested samples of bread were analyzed using two mothed (qualitative and quantitative analyses) a spectrophotometric method of bromate analysis. Bromate concentrations ranged from 0.07-0.29 μgg^{-1}, with an overall mean concentration of 0.14±0.07 µgg-1(ppm). Significant differences were noticed.

تحليل لمحتويات بروومات البوتاسيوم لأرغفة الخبز الشائعة الاستهلاك في مدينة توكره- ليبيا

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الكلمات المفتاحية:
الخبز
المظافات الغذائية
المواد المسرطنة السمومية
العامل المؤكسد
بروومات البوتاسيوم
مقياس الطيف الضوئي للأشعة المرئية
وفوق البنفسجية

الملخص

خلال القرن الماضي، تم استخدام بروومات (KBrO3) كعامل مؤكسد قوي علي نطاق وأسع في عمليات صناعة الخبز، هذه المواد لها العديد من الآثار الضارة علي القيمة الغذائية للخبز، صنفت أيضاً من قبل الوكالة الدولية لأبحاث السرطان (IARC) على أنها مادة مسرطنة للإنسان ومطفرة (تسبب تغير فى البيئة الجينية). لهذا السبب تم حظر استخدام بروومات البوتاسيوم في الخبز ومنتجات المخبوزات الأخرى في العديد من البلدان حول العالم. حيث حددت وكالة الغذاء والدواء الأمريكية (FDA) تركيز 0.02 ميكروغرام/غرام كحد أمن مسموح به لبروومات البوتاسيوم فى الخبز. لذلك أصبح من الضروري تحديد محتوي مادة بروومات البوتاسيوم في عينات الخبز المختارة في منطقة الدراسة (توكره- ليبيا). في هذه الدراسة، تم فحص 21 عينه من الخبز من مختلف المخابز في توكره. أولا؛تم إجراء التحليل النوعي والذي يعتمد علي وجود لون مرئي ناتج عن تفاعل البروومات مع اليوديد (محلول يوديد البوتاسيوم) ومن ثم إجراء التحليل الكمي لقياس تركيز البروومات فى جميع العينات باستخدام طريقة القياس الطيفي. أثبتت هذه الدراسة أن جميع العينات التي تم تحليلها تحتوي على مستويات مختلفة من بروومات البوتاسيوم، وتجدر الإشارة إلي أن أقل تركيز كان 70.0 ميكروغرام/غرام وأعلى تركيز كان 0.29 ميكروغرام/غرام وكل التراكيز كانت أعلى من الحد المسموح به وهو 0.02 ميكروغرام/غرام وهو ما يعتبر مهدد للحياة البيئة وغير أمن للاستهلاك البشري.

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Introduction

The Bread is the one of the oldest man-made foods. With the evaluation of human bread it evolved, and with different human needs, bread types would differ according to human needs, such as health conditions and taste preferences) [1].

Potassium bromate, is an oxidizing agent and one of the best and cheapest dough improvers in the baking industry. Due to its positive effects, it plays a major role in the bread-making industry. Potassium bromate has significant effect on food biomolecules, such as starch and protein, as it affects the extent of gelatinization, viscosity, swelling characteristics as well as gluten proteins; it removes the sulfhydryl group and leads to the formation of disulfide linkages and thus improves the bread properties [2]. It is a slow oxidizing agent acting on gluten protein to increase loaf volume and to create a good texture of the bread [3],[4]. During the bread baking process, potassium bromate is reduced to potassium bromide, which is safe for human health. However, use of excessive potassium bromate may result in residual bromate left in the bread, potentially having harmful effects on the consumer [5],[6].

Bromate has been classified by the International Agency for Research on Cancer (IARC) as a possible human carcinogen, it has been removed from the list of acceptable additives for flour treatment in several countries such as France, UK, and Canada [5],[7]. In Japan and China, maximal permitted doses of potassium bromate in bread are 10 and 20 mg/kg of flour mass, respectively [8]. In the USA, a maximum residual concentration of 20 parts per billion (ppb) is allowed within the finished bakery products [8]. In 1982, researchers in Japan published the first of a series of studies showing that potassium bromate causes cancer in the thyroids, kidneys and other body parts of rats and mice. As a result of these findings, countries around the world banned the additive, but the U.S. Food and Drug Administration held back, in part because the amount of potassium bromate that remains in bread after baking should be negligible: less than 20 parts per billion (ppb= µg/g).According to information published by baking industry trade groups, it is "well within the normal production control measures in any modern bakery to ensure that bromate residues are well below 20 ppb". However, whenever bromated flour isn't baked for long enough or at a high enough temperature, or if too much potassium bromate is added in the first place, this harmful additive can potentially be found in the final product in far greater quantities) [10].

Today, many small and commercial bakeries voluntarily avoid using bromated flour. However, it's still found in many fast-food buns and some flours, among other products. In Tokra, the use of potassium bromate as a food additive is not controlled. Tokra breadmaking is regulated by standard NT 51 82 (NT51.82 1999) with two added standards: NT 117.01 (NT117.01 1995) regarding the use of additives and NT 51 25 (NT51.25 1999), regarding the use of baker's yeast. As bread is the food item most consumed by the Toka population, with an annual intake of about 70 kg per person (NIS 2013), it is crucial that the levels of residual bromate in Tokra breads be determined.

The main objective of this study was to evaluate the potassium bromate contents in commonly consumed loaves of bread samples in Tokra city and its environs in Libya as most of these product's labels only indicates the nutritional attributes and not their safety which is taken for granted in developing countries.

Experimental Work

1. Materials and Method

1.1 Survey and collection of bread samples A survey of available loaves of bread samples in Tokra, Libya, were carried out in bakeries located in the city and its suburbs. Twenty-one samples of seven different types of bread freshly baked and well packaged by their bakers were selected based on their availability and popularity among most of the consumers. The bread samples are represented with WB1to WB7.

1.2 Chemicals all chemical and reagents used in this study were of analytical grade and were purchased from qualified companies. Potassium Bromate (Sigma chemical Co, St Louis, USA), Potassium iodide (Sigma chemical Co, St Louis, USA), Sodium hydroxide (Hopkins and Williams Ltd, England). De-ionized water was used for all solution preparations and dilutions. All glassware containers were cleaned by prior overnight soaking in diluted HNO3 (10%) before a final rinse with distilled water. Potassium iodide solution (0.5%) was prepared by dissolving 0.5g of iodate-free potassium iodide solid in 100 mL 0.1N hydrochloric acid solution.

1.3 Apparatus

All the absorbance measurements were carried out using a single beam Spectrophotometer (UV-VIS Spectrophotometer SPECORD 40. Analytik Jena Germany) with 1.0 cm matched cells. The analysis of bread and baked products samples were carried out in Chemical Analysis Laboratory of Chemistry Department in Tokra city, University Benghazi.

1.4 Procedure

1.4.1Estimation of the level of Potassium bromate (Calibration Curve)

The mean absorbance produced by the standards (corrected for the standard blank) was plotted versus the concentration of the analyte in the sample to produce a calibration curve Fig. (1). The concentration of potassium bromate in each bread sample was calculated using the equation of the calibration curve based on its absorbance.

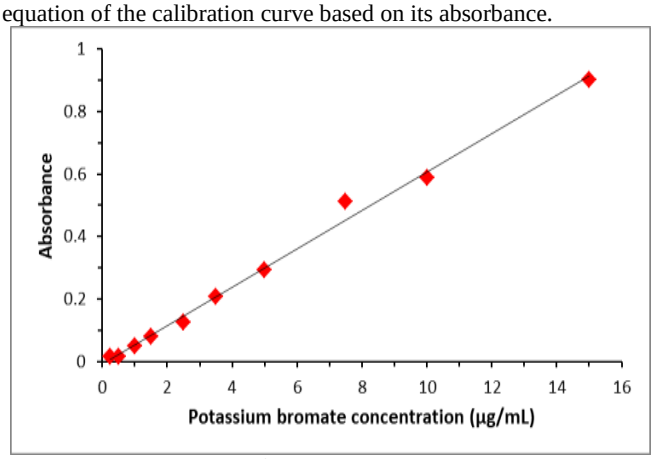

Fig1: The standard curve of potassium bromate (0.01-15 µg/ml) using potassium iodide solution. The absorbance is measured at 520 nm. The linear regression equation is A = 0.061 C + 0.009, (R^2 = 0.994).

1.4.2 Qualitative analysis

Sample analysis

Qualitative tests were performed directly on apportion of each bread sample with 2mL 0.01M of promethazine and 0.6 mL of 12 M HCl. Qualitative determination of bromate content in the bread samples was reacted with potassium iodide to produce the bromine ion.

The product colour ranged from light to dark pink as the concentration was increased. The degree of colour change correlates with the level of potassium bromate present in the sample [13].

1.4.3 Quantitative analysis

Determination of potassium bromate in bread samples Potassium bromate contents of the bread samples were analyzed using previously reported method [11]. 1.0 g was weighed out from each bread sample in an electronic weighing balance and was transferred into a test tube. 10 ml of distilled water was added, and the mixture was shaken and allowed to stand for 20 min at 28 ± 5°C. 1.0 ml was decanted from the test tube into another test tube and 1.0 ml of freshly prepared 0.5% potassium iodide solution in 0.1N hydrochloric acid was added. Any colour change was noted. The presence of potassium bromate was indicated by change in colour from light yellow to orange [11]. The absorbance of the sample was detected using ultraviolet visible spectrophotometer (UV/VIS) at maximum wavelength, (λ_{max}520nm).The concentration of bromate was calculated from the linear regression curve obtained from the working standards. Absorbance of the sample was converted to concentration with reference to Beer's calibration curve previously constructed for potassium bromate using the pure sample [12]. The represeponding regression equation of the calibration curve prepared from the standard solution of potassium bromate (µg/g) in each sample is calculated, using equation (1).

Con. $KBro_3$ (µg/g) =

$$\left(\frac{Con.\ KBro_3\ \mu g/mL}{sample\ weigh(g)}\ \text{X dilution factor}\right)\text{…….....…...}\textbf{Eq. (1)}$$

2.Statistical analyse

The data of experimental analysis were done in triplicate determinations. The results are expressed as(µg/g) (ppm) mean ± sd. Readings were compared using the one-way ANOVA analysis and independent sample test. Statistical analysis was performed using Social Analysis SPSS (Version 17), assuming that there were significant differences among them when the statistical comparison gives a a level of p <0.05 was, the post-hoc analysis was done through the least significance difference (LSD).

Result and discussion

In this study, the concentration of bromate in the collected baked samples from the city of Tokra and its environs, that have collected in February 2023, were determined by spectrophotometric method, that based on the reaction of bromate ions with iodide ions in acid medium to produced iodine, as shown in equation (2).

The produced iodine formed blue colour complex in presence of starch from baked products [12].

$$BrO_3^- + 6I^- + 6H^+ \rightarrow 3I_2 + 3H_2O + Br^- \text{ .....…}\textbf{Eq. (2)}$$

Potassium bromate in bread samples analyzed is shown in (Table 1). The sample with the lowest concentration of potassium bromate was detected in sample WB4 (0.07µg/g), whereas the highest concentration was found in sample WB1 (0.29 µg/g).

Table 1: Potassium bromare concentrations in bread samples collected from different bakeries in Toukra city, n=3, (mean ±sd)

Sample Code	Potassium bromate Content (µg/g) ppm
WB1	0.29±0.04
WB2	0.13±0.02
WB3	0.12±0.02
WB4	0.07±0.01
WB5	0.13±0.03
WB6	0.08±0.02
WB7	0.14±0.01
Mean ±sd	0.14±0.07
Range	(0.22)
Min- Max	0.07-0.29
Permissible level (FDA)	0.02
WHO	0.025

These levels are higher than 0.02µg/g, permitted by the US Food and Drug Agency [14], but it's much lower than the levels detected of some studies of cities in Libya as Tajora region in Tripoli city, the range of potassium bromates concentration for 25 bakeries was (6.0-26.67µg/g), in Benghazi city was (0.19-1.84 µg/g), and in Tobruk city the rang of the values potassium bromate was (1.70- 6.21)[15-18]. These high concentrations agree with other findings which were recorder in some neighbouring countries such as Tunisia and Morocco, the concentration range of potassium bromate in bread samples were (5.95-49.31 µg/g) and (4.99- 12.32 µg/g) respectively [19], [20]. However, our results are somewhat close to the results of the study that was applied to bread samples that were collected from markets in Saudi Arabia (0.15- 0.46 µg/g) [21].

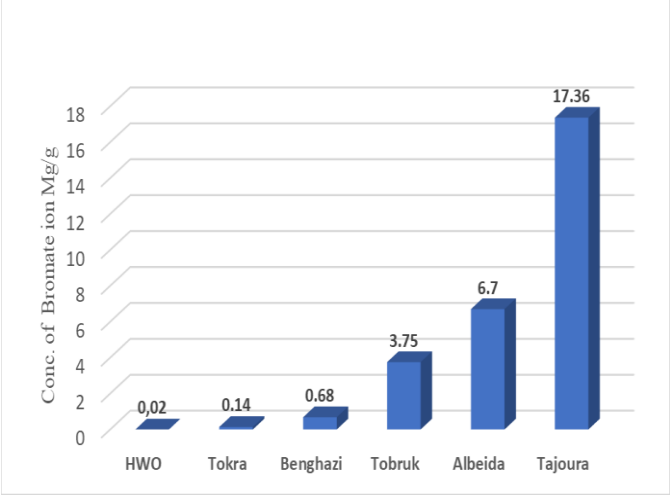

Fig2: Comparative the mean concentrations(µg/g) of potassium bromate in some bread samples between different studies cities in Libya, with the maximum allowed limit recommended by who.

Fig. (2) showed that the comparison the mean of concentration of potassium bromate in our study with the mean concentration of studies of another Libyan cities; it is clear the lowest mean concentration of the potassium bromate in bread sample detected in Tokra city, although this level is greater than the limited value (0.02 µg/g) [2], [14].

The concentration of potassium bromate standard used in spiking for constructing calibration curve includes 0.010-15µg/mL. The calibration curve based on concentration versus absorbance at 520 nm is drawn using excel Fig (1). The slope, intercept, and correlation coefficients of the calibration curve for potassium bromate are 0.061, 0.994, respectively. The method detection limit of potassium bromate was found to be 0.01.

Results showed that bromate concentrations in the Tokra breads tested ranged between 0.07 and 0.29 µg g^{-1}(ppm) with an overall mean concentration of 0.14±0.07µg g^{-1}. Considering the maximum residual.

Potassium bromate was found in all samples and it has been found at a concentration above the limit set World Health Organization, and Food and Drug Administration. The level of potassium bromate in the studied samples against the number of folds more than international limits is presented in table (1).

In the bread samples, the average contents of potassium bromate in samples collected from Tokra, Libya was 0.14 ±0.07 µg/g. In Tokra city is n't safe for human consumption, there are two ways by which humans may get poisoned with potassium bromate; by ingestion when it is present in food such as bread or by inhalation. It is therefore, not safe for bread consumer and the bakery workers where the substance is used as a bread improver [23].

Conclusion

In this study of the tested samples contained high levels of residual potassium bromate above the permissible level. This confirms that potassium bromate is still used in Bakeries in Tokra city and indeed in Libya, despite its ban since 2005 [23].

The lowest quantity of potassium bromate in WB4 (0.07±0.01µ g/g) was detected and the highest level of bromate in WB1 (0.29±0.04 µ g/g) was found in the sample collected from Tokra city.

Bread consumers and bakers in Tokra city are at threat of exposure to potassium bromate with health implications. This announces for strict action to be taken by relevant authorities to reaffirm the proposed ban. Routine checks should be implemented to ensure that bakeries always comply with the safety guidelines. Bread makers should use alternative flour improvers that are safer to human.

Recommendation

Until very recently, Potassium bromate is a flour improver that strengthens dough and allows the dough to rise higher during baking. Usually 0.02 µ g/g of potassium bromate is used during the flour

treatment stage. Ideally, the act of baking changes its chemical composition and thus leaves no trace in the finished product.

And, if too much of the additive is used, or the bread is not baked long enough or at optimal temperature, then a residual amount will endure.

Therefore, Bread makers and Bakers are officially advised against the use of potassium bromate as bread improver. They should use alternative bread improvers such as:

- Yeast Ascorbic acid or Vitamin-C: Ascorbic acid, also known as vitamin C, is an essential nutrient found in citrus fruits. The use of this acid in bread dough in the range of 20-30 mg/ kg of flour increased bread volume by 20% [25]. it may be from natural or synthetic sources.
- Glucose oxidises: The use of enzymes is the best alternative to chemical compounds because they are generally recognized as safe and do not remain active after baking. One of the enzymes that can confer strength to the dough is glucose oxidise.
- Other food improvers and flour treatment agents include ammonium. persulphate, ammonium chloride and amylases [26]

In a recent study showed, that the aqueous extract of Hibiscus sabdariffa (calyx) is antioxidant and antimicrobial activities, highlighting that the hydroethanolic extract presents not only lipid peroxidation inhibition capacity, but also bactericidal/fungicidal inhibition ability for all the bacteria and fungi tested. Furthermore, both extracts revealed the absence of toxicity using porcine primary liver cells. The studied plant species was thus not only interesting for nutritional purposes but also for bioactive, colouring applications in food, cosmetic and pharmaceutical industries and it has its effective in reducing toxicity as potassium bromated and another antioxidant [27], [28].

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