



Determination of the Concentration of Potassium Bromate and Some Heavy Metals in Some Bread and Pastry Samples

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Abstract

Food additives: are compounds that are added to food to maintain flavor or improve its appearance, taste, or other sensory attributes.

Potassium Bromate: Bakers regularly employ potassium bromate (KBrO_3) as an oxidizing agent to improve bread quality. It improves gas retention and product volume by maturing flour and strengthening the gluten network. IARAC in 1999 classed it as a category 2B carcinogen (probably harmful to humans). The main aim of this study is determination the contents of potassium bromated in some Bread and Pastry products collected from different cities in Libya.

Sampling: Total different fifty samples of bread and pastry products were collected randomly from local markets from some Libyan cities.

Mythology: The absorbance of the samples was measured at 620 nm using a UV-V by spectrophotometer. Analysis was done on three replicates for each of the samples.

Results: All of the 50 samples show a high level of KBrO_3 ranged from (2.632-16.54 $\mu\text{g/g}$).

Discussion: The results of the contents of potassium Bromate in the studied samples showed wide variations. Potassium bromate was found in all samples and higher than the limits which set by World Health Organization (WHO), and Food and Drug Administration (FAO).

Conclusion: According to the obtained results in this study there is wide variations in the potassium bromated contents, where some of samples contained high values given by WHO and FAO presimble limits. There are some heavy metals values higher than the WHO and NHMRC guide lines for human consumer

1. Introduction:

Bread is a staple diet for the majority of the world's population, and it's often created with flour and other ingredients to enhance its varied features. One of these materials is potassium bromate, which is used to improve the appearance, texture, shape, and size of bread. However, there is much debate about the health risks of potassium bromate, which include kidney failure, hearing loss, respiratory difficulty, and the development of various cancers. There are numerous analytical methods for determining potassium bromate, but they are all difficult, costly, and time-consuming. (Afolabi *et al.*, 2015).

Additives in bread making

The main classes of additives used in breadmaking are: (i) oxidants/reductants;(ii) emulsifiers;(iii) hydrocolloids; and (iv) preservatives.

Bakers regularly employ potassium bromate (KBrO_3) as an oxidizing agent to improve bread quality. It improves gas retention and product volume by maturing flour and strengthening the gluten network. By oxidizing the sulfhydryl groups of the gluten protein in flour into di sulphide bridges, KBrO_3 works as a maturing agent and dough conditioner, making the dough less extensible and more elastic. This makes the dough viscoelastic, allowing it to retain the carbon dioxide gas created by the yeast. (IARAC,1999).

Potassium bromate has a general impact of improving bread texture and increasing loaf volume. Based on substantial evidence that potassium bromate KBrO_3 causes cancer in experimental animals, the International Agency for Research on Cancer classed it as a category 2B carcinogen (probably harmful to humans). (IARAC,1999), Many nations throughout the world have banned bromate in flour and bakery items as a result of this discovery, Sri Lanka prohibited the chemical in 2001, Nigeria banned it in 2004 (Ekop *et al.*, 2008), China banned it in 2005, and India banned it in 2016. Countries such as the United States of America have set maximum limitations for the use of KBrO_3 as a food additive rather than outright bans. The highest potassium bromate content allowed in bread by the US (FDA) is 0.02 $\mu\text{g/g}$ (0.02 mg/kg) (Ekop *et al.*, 2008).

Aim of study:

The main aims of the current study can be summarized in the following points:

1. Determination the contents of potassium bromate in some Bread and Pastry products collected from different cities in Libya.
2. Estimation the contents of some metals (Fe, Cu and Ni).
3. Calculation of some of validation parameters of the methods of analysis.

2. Methodology:

Sampling:

Total different fifty samples of bread and pastry products were collected randomly from local markets at some Libyan cities, the samples were included local and imported different types of pastries. In this study the samples were subjected as following:

Table (2.1): The studied samples:

Sample	type	Sample	type
1	toast	26	bread
2	croissant	27	bread
3	pancake	28	bread
4	bread	29	bread
5	bread	30	bread
6	bread	31	bread
7	bread	32	bread
8	bread	33	bread
9	bread	34	bread
10	pancake	35	biscuit
11	bread	36	biscuit
12	bread	37	croissant
13	bread	38	croissant
14	croissant	39	croissant
15	bread	40	croissant
16	bread	41	croissant
17	bread	42	croissant
18	bread	43	croissant
19	pancake	44	croissant
20	toast	45	pancake
21	croissant	46	croissant
22	bread	47	pancake
23	bread	48	croissant
24	bread	49	croissant
25	bread	50	croissant

2.2. Preparation of standard solutions of potassium bromate:

The concentration of $KBrO_3$ standards used calibration curve including :1, 2, 3, 4, and 5 $\mu\text{g/ml}$. The calibration curve based on concentration versus absorbance is drawn using excel. The slope, intercept and correlation coefficients of the calibration curve for potassium bromate were calculated and the unknown concentrations were calculated from the regression equation.

2.3. Samples preparation:

Potassium bromate in the bread samples was qualitatively and quantitatively analyzed using reported methods (Nnaji *et al.*, 2010.). A 1.0 g quantity was weighed out from each bread sample using an analytical weighing balance. This was transferred into a test tube. (10 ml) of distilled water was added; the mixture was shaken and allowed to stand for 20 min at $28 \pm 10^\circ\text{C}$. Heating was done using a water bath and the temperature of the mixture was controlled using a thermometer. After cooling, a 5.0 ml volume was decanted from the test tube. A 5.0 ml quantity of freshly prepared 0.5% potassium iodide solution in 0.1N hydrochloric acid was added. Any color change was noted. The presence of potassium bromate was indicated by a change in color from light yellow to purple. The absorbance of the samples was measured at 620 nm using a UV-V by spectrophotometer. Analysis was done on three replicates for each of the samples.

2.4. Preparation of standard solutions of iron, copper and Nickel:

The standard solutions of the selected heavy metals in study were prepared by dissolved the calculated amounts of each metal chlorides of (FeCl_3 , NiCl_2 and CuCl_2) in 100 ml of distilled water, then the working solutions were (1, 2, 3, and 5 $\mu\text{g/ml}$). The modified methods were used in this study to estimate the selected heavy metals by spectrophotometer at the central Lab of Chemistry department, Omar Al-Mukhtar University.

2.4.1. Digestion of the Samples for Heavy Metals Determination:

For the determination of selected heavy metals, about 0.5 g of homogenized sample was weighed and transferred into a (100-ml) beaker then 5 ml of concentrated HNO₃ was added. Samples were digested according to the procedure used by (APHA, 1958). On a hot plate in the digestion chamber (fume hood), 0.5 g of finely ground powder was wet digested in a 100-ml conical flask by adding a 3 ml mixture of distilled water and 5 ml of nitric acid (HNO₃) in a ratio of 3%. Heating and digestion continued until the liquid became colorless or bubbles appeared. The liquid was further heated to a volume of 2-3 ml, then lifted aside to lose the heat. Leave the solution to cool, then dilute with distilled deionized water in a 100 ml volumetric flask. Finally, the diluted sample is filtered by the filter paper and stored in a polyethylene bottle for measuring heavy metals.

2.5. Validation Calculations:

Some of validation calculations were used in this study including: Linearity, Correlation values, Linearity, Limit of detection (LOD), limit of quantification (LOQ).

3.Results and Discussion:

3.1. The results:

The results which obtained from this study can be description according to the concentrations of potassium bromate (KBrO₃, Fe, Ni and Cu) as following:

Potassium Bromate Concentrations:

The concentrations of potassium bromate in this study are shown in the following Tables (3.1-3.5) and Figures of (3.1- 3.5), where the concentrations were fluctuated in the ranges of: (2.632-14.096 µg/g), (9.69 -10.92 µg/g), (4.41 -15.50 µg/g), (1.75 -3.43 µg/g) and (3.95 -16.54µg/g) for the bread, biscuit, croissant, toast and pancake, respectively.

Table (3.1): The concentrations of KBrO₃ for the samples of (1 – 10).

Sample	Ppm
1	11.19
2	13.87
3	5.66
4	14.09
5	3.43
6	11.81
7	5.43
8	6.93
9	8.60
10	3.95
Average	8.49
±SD	4.00

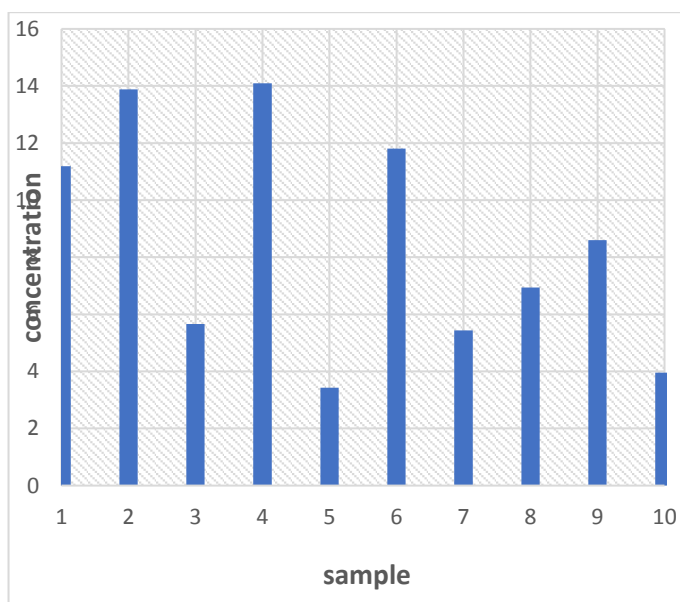


Figure 3.1. The potassium bromate concentrations in samples of (1-10).

Table (3.2): The concentrations of KBrO_3 for the samples of (11 – 20).

sample	Ppm
11	12.07
12	11.12
13	9.49
14	12.39
15	5.39
16	6.09
17	10.96
18	13.19
19	16.54
20	3.43
Average	10.06
\pm SD	4.01

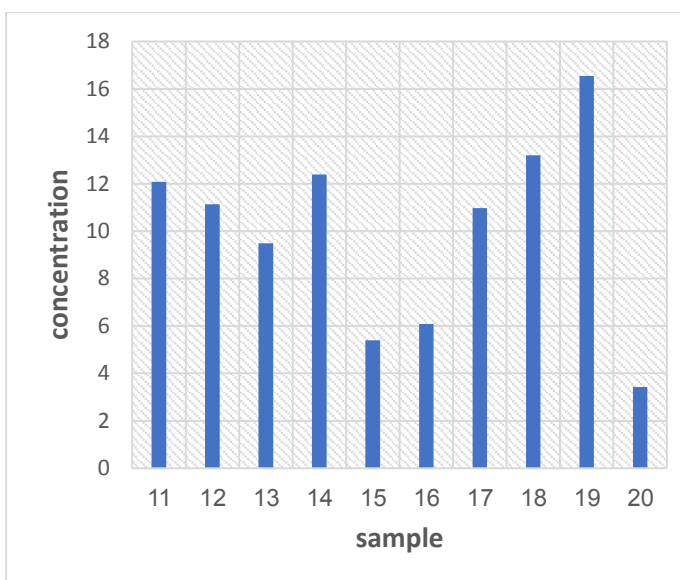


Figure 3.2. Showed a Comparison between potassium bromate concentration in samples (11-20).

Table (3.3): The concentrations of KBrO_3 for the samples of (21 – 30).

sample	ppm
21	4.41
22	5.55
23	9.76
24	11.22
25	2.63
26	6.59
27	6.97
28	6.20
29	5.29
30	10.01
Average	6.86
\pm SD	2.70

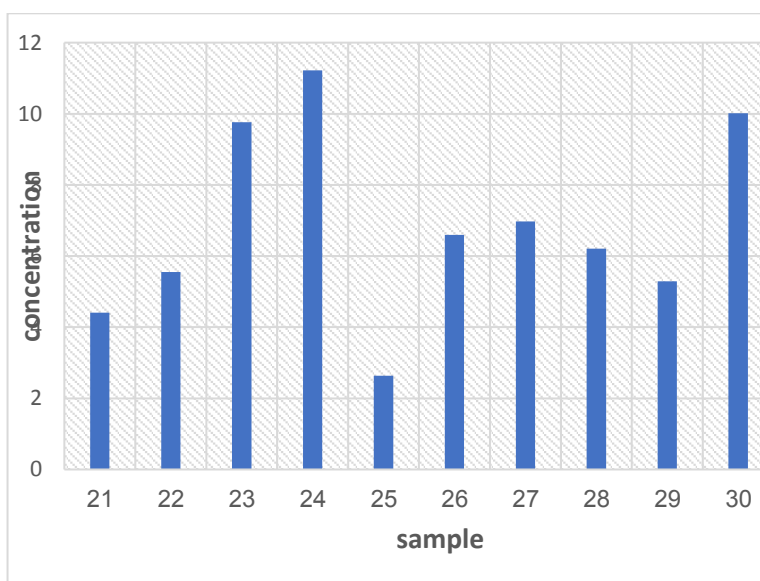


Figure 3.3. Showed a Comparison between potassium bromate concentration in samples (21-30).

Table (3.4): The concentrations of KBrO_3 for the samples of (31 – 40).

sample	ppm
31	13.28
32	13.83
33	11.18
34	12.14
35	10.92
36	9.69
37	13.90
38	5.22
39	7.28
40	10.38
Average	10.78
$\pm\text{SD}$	2.82

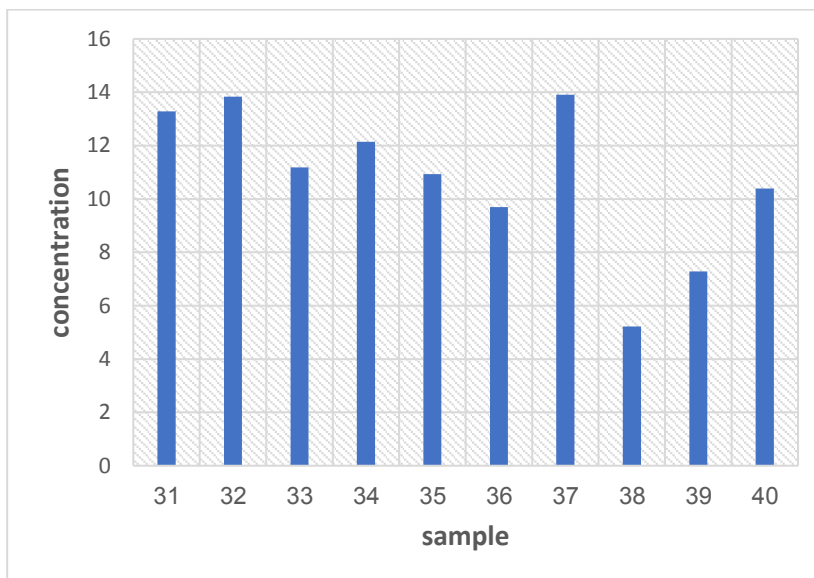


Figure 3.4. Showed a Comparison between potassium bromate concentration in samples (31-40).

Table (3.5): The concentrations of KBrO_3 for the samples of (41 – 50).

Sample	Ppm
41	5.38
42	10.87
43	14.90
44	11.83
45	11.83
46	15.37
47	16.52
48	10.61
49	15.50
50	14.79
Average	12.76
$\pm\text{SD}$	3.36

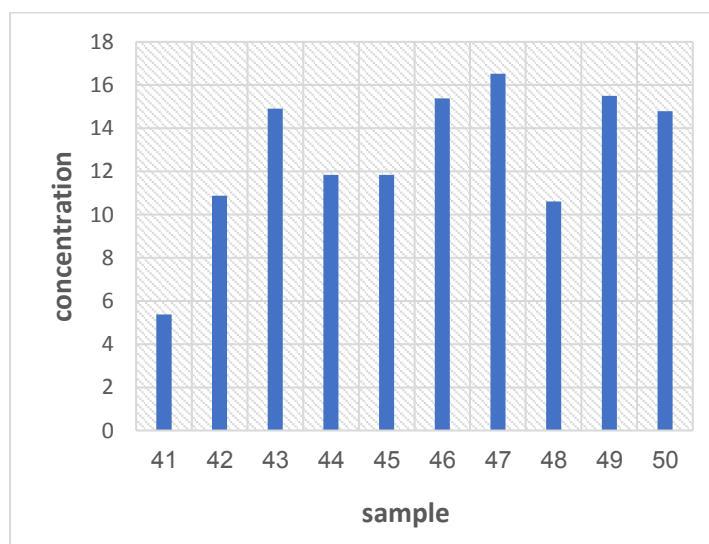


Figure 3.5. The potassium bromate concentration in samples of (41-50)

.Heavy metals:

1. Iron

It is an essential trace element required by all forms of life. In man, it is required for the synthesis of hemoglobin and in many enzyme systems. Various groups (male, female, children, pregnant, lactating) differ in the requirement for iron, iron deficiency is one of the most common nutritional deficiencies in children, women of childbearing age, and pregnant women. It rarely occurs in adult men, except in cases of chronic bleeding. The concentrations of iron in the bread samples of this study were ranged between (0.020-0.160 µg/g). The permissible limit for Fe in food is in the range of (2.5-5.0 µg/g) depending on the food stuff (CAC), (2003). The bread samples of this had iron concentrations below the permissible levels. However, in humans, acute toxicity of iron ingested from normal dietary sources has not been reported.

2. Copper:

According to WHO guidelines the allowable concentration of copper for human consumption is 30 µg/g for the results it appears that the concentration of copper in all studied samples are below the acceptable safety ranges. These concentrations are far above the permissible level of Cu in foods (10 ppm). The samples can therefore be considered to have Cu contamination.

3. Nickel:

Nickel is also extensively bioaccumulated from the intake of contaminated food (Singh and Ferns, 1978). In this study, it was found that the selected samples showed an accumulation of Ni in all the samples. Some studies indicated that Ni is toxic for humans at high levels (Tjalve *et al.*, 1988). The Estimated maximum guideline (USFDA, 1993) for Ni is 5 µg/g. Thus, the concentrations of Ni in all the samples were ranged between (0.047-0.079 µg/g). and below the stipulated limits.

Metal containers used for kneading dough during bread-making may be responsible for high levels of such metals. 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. Figure (shows possible sources of heavy metal contamination during bread production (Magomya *et al.*, 2013).

3.2 Discussion:

The results of the contents of potassium Bromate in the studied samples showed wide variations. Potassium bromate was found in all samples and higher than the limits which set by World Health Organization (WHO), and Food and Drug Administration (FAO).

The average contents of KBrO₃ in samples was (9.79 ± 3.37). The contents of potassium bromate were ranged between (2.632 – 16.54 µg/g), by comparing the obtained values of potassium bromate in this study with the values of studies carried out in Nigeria (1-16 µg/g) and (1.16 - 10.44 µg/g) (Emeje *et al.*, 2010) and (Okolie and Osartenren ,2003). This study recorded high levels of potassium bromate than those recorded in Nigeria (1.08- 3.78 µg/g) in some bread samples (Ekop *et al.*, 2008).

It was reported that potassium bromate is used as a flour improver has been in the use for more than 80 years. The use of PB has been a popular choice because it is cheap and probably the most efficient oxidizing agent (Zhou and Hui,2006). It makes the bread stronger and more elastic, and also promotes big rises of bread. The resulting bread tends to be strong and springy, and especially well-suited to commercial production (Vadlamani and Seib,1999).

The maximum amount of potassium bromate allowed in bread by the FDA is 0.02 (µg/g). All the samples analyzed in this study had potassium bromate in excess of the allowed concentrations. Similar Studies by carried out revealed similar findings (Magomya *et al.*, 2013). The presence such levels of potassium bromate in bread is highly undesirable considering its deleterious effects.

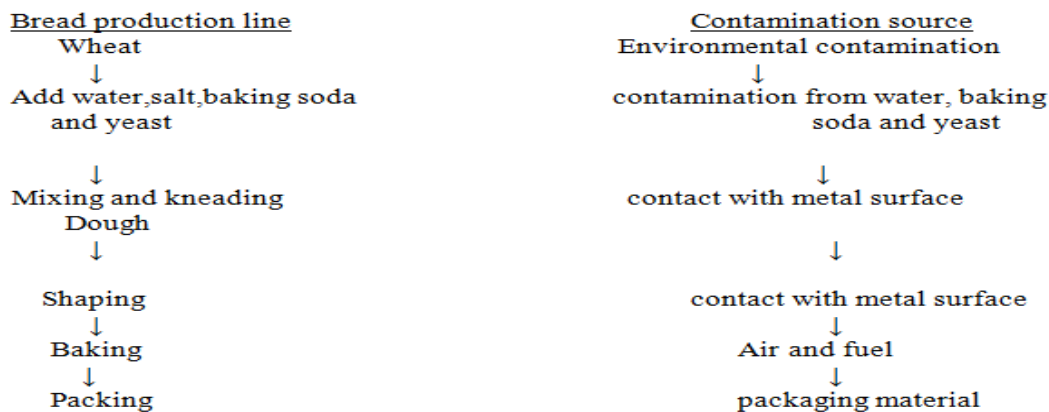


Figure (3.3). Possible sources of heavy metal Contamination during bread production

3.3. The validation of the methods of analysis.

The validation the methods of analysis of potassium bromated and the studied heavy metals was carried according to different calculations including:

Linearity, Correlation coefficient, Limit of Detection (LOD) and Limit of qualification (LOQ). The data are the illustrated in Table of (3.3) and Figure (3.3).

Parameter	KBrO ₃	Iron	Nickel	Copper
Linearity	1-5 µg/ml	1 -5 µg/ml	1 -5 µg/ml	1 -5 µg/ml
Regression	$Y = 0.155 X + 0.023$	$Y = 0.0334X - 0.0012$	$Y = 0.0844 X - 0.045$	$Y = 0.0062 X - 0.0015$
Correlation	0.99	0.99	0.99	0.99
LOD	0.32	0.808	0.562	0.454
LOQ	1.09	2.69	1.87	1.51
Slope	0.155	0.0334	0.0844	0.0062

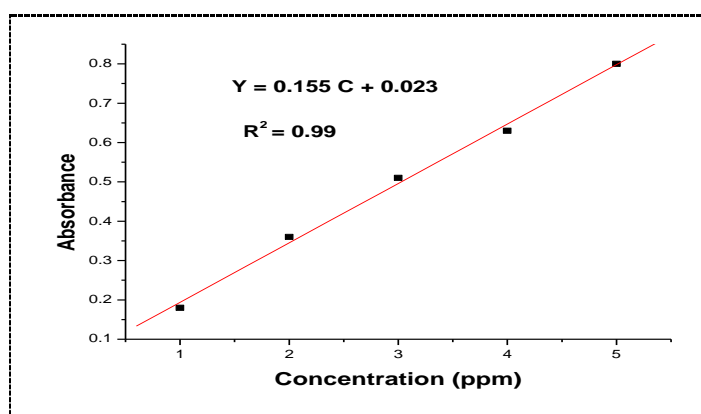


Figure (3.3): The standard curve of potassium bromate.

3.4 Conclusion:

According to the obtained results in this study which carried out on the bread and some of pastry samples collected from different markets at some Libyan cities, there is wide variations in the potassium bromated contents, where some of samples contained high values given by WHO and FAO presimible limits. There are some heavy metals values higher than the WHO and NHMRC guide lines for human consumer.

A study of other metals which not carried out in this study. Select other types of pastries to determine the other heavy metals.

Recommendations:

There are many methods which can be using to estimate the heavy metals and potassium bromated m therefore using other methods to determinate other heavy metals is highly recommend in other studies and /or select other instruments as Atomic Absorption and X-Ray analysis.

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