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#### Detection of Potassium Bromate as an Improver in Breads Produced in Some Bakeries in Benghazi, Libya

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Abstract: Bread is considered the basic and indispensable food in all parts of Libya, and for all social and economic groups. Potassium bromate (KBrO3) is a colorless, odorless and tasteless white crystal/powder that is used as a food additive in the pastry industry to improve the functionality of dough as an oxidizing and bleaching agent. After many long-term studies, in 1999 the International Agency for Research on Cancer (IARC) classified potassium bromate as a potentially carcinogenic compound (Group 2B), and officially in 2012, the Codex Alimentations Committee withdrew the specification of potassium bromate as an additive. The aim of this study to check whether the Libyan bread particular, the Benghazi bakeries is free of potassium bromate. Sixty different types of bread samples were randomly collected from 60 different bakeries in the city of Benghazi, three flour samples and four bread improvers were also collected from different supermarkets. The qualitative (black spot test) and colorimetric quantitative methods to detection on presence potassium bromate was done. All result of this study recorded negative potassium bromate level (0.00 ppm) in 60 bread samples, the results showed also all flour samples and improvers are free of potassium bromate. In conclusion, all samples were completely free of potassium bromate and this confirms that potassium bromate was not used in bakeries in Benghazi, Libya, which has been banned since 2005.

Key words: potassium bromate, bread, improvers.

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#### Introduction:

Throughout Libya, among all social and economic groups, bread made from wheat flour considered the staple and indispensable food. Potassium bromate (KBrO3) is a colorless, odorless and tasteless white crystal/powder that is used as a food additive in the pastry industry to improve the functionality of dough as an oxidizing and bleaching agent (The World Heath Organization, 1995). It works to strengthen the gluten network of wheat flour doughs, improve the ability of the dough to retain gas, increase its elasticity and rheological properties. Potassium Bromate is usually added to flour to make it stronger and more flexible when kneading, as an oxidizing agent, it oxidizes the thiol groups of flour gluten and works to form disulfide bridges between gluten molecules. As a result, this effect leads to improved texture and a significant increase in bread volume during the baking process (Rosentrater, K.A,2018). It seems clear that the role of potassium bromate as an improver for baked goods is related to the texture property, as it increases the cohesion of the gluten network and improves the viscoelastic balance of the dough, which facilitates and speeds up the kneading process. It occurs as previously said thus of the formation of disulfide bonds between gluten molecules, which makes them stronger and agglomerated, which helps to increase the ability of the gluten network to hold the gas formed during the baking process (Sahi, S.S, 2014).

The addition of potassium bromate may also affect some other components of flour such as protein and starch, as it has an effective effect on increasing the ability of these components to form a gel, as well as improving its viscosity and ability to swell. On the other hand, bromate may be present in ozonetreated drinking water as a sterilization method, where ozone (O3) reacts with bromide, which is naturally present in the water, to form bromate. In addition, exposure of water containing bromide to sunlight encourages liquid or gaseous bromine to form bromate (photo activation).

In view of the cheap price of potassium bromate and its wide availability compared to other food additives, and its good results for the final product, many countries have encouraged it to use as a improver in bread industry previously. As a low cost and high quality are required in such industries (American Bakers Association (ABA) and AIB International. "Commercial Baking Industry Guide, 2008). The study of the harmful effects of potassium bromates as a bread improver began in 1948, the studies showed the harmful effect on the nutritional value of bread, as it leads to a decrease in the value of vitamin B2, B1, A2, and niacin, which are important vitamins in bread. Studies have also

confirmed that eating a large amount of bromate leads to the emergence of symptoms of poisoning in the digestive system, such as nausea, vomiting, diarrhea, and abdominal pain, and in some people may lead to injuries of the kidneys and nervous system, pain and hearing loss. Chronic consumption of bromate leads to kidney failure and cancer in experimental animals, and the same effect may occur in humans (International Agency for Research on Cancer, 1990). Since 1914, potassium bromates began to be used in the bread industry as a ripening agent and flour improver under No. E924, and in 1941 potassium bromate was approved as a bread improver by (FDA) at a rate of 50 mg/kg flour. Then, in 1952, the utilization rate was raised to 75 mg/kg flour. In 1964 the World Health Organization (WHO) and the Food and Agriculture Organization (FAO) began conducting evaluation studies on potassium bromate (U.S. Food and Drug Administration, 2018).

Based on the results of the World Health Organization and the Food and Agriculture Organization in 1983, the recommended level of potassium bromate in the baking industry was established at 75 mg/kg of flour under the heading (Provisional approval), since it is assumed that only a small part of the compound is remained in the product, where most of it turns into bromide during the baking process which is less dangerous. This rate has been reduced to 60 mg/kg after a lot of studies. Afterward, in 1992 and after several studies, the Subcommittee on (WHO) and (FAO) classify the use of potassium bromate in the baking industry as "not appropriate" and other alternatives were put in place of it. In 1999 the International Agency for Research on Cancer (IARC) classified potassium bromate as a potentially carcinogenic compound (Group 2B),

and officially in 2012, the Codex Alimentations Committee withdrew the specification of potassium bromate as an additive (<u>International Agency for</u> <u>Research on Cancer, 2008</u>).

Among the first countries to ban the use of potassium bromate as a flour improver, where the European Union, China, South Korea, Sri Lanka, Canada, Australia, Brazil, Peru, Colombia. As for the United States and India, they did not prohibit the use of potassium bromate as an enhancer at low rates of 50 mg/kg flour in India and 75 mg/kg flour in the United States, if it is written on the label that the product contains potassium bromate.

#### Aim of Study:

To check whether the Libyan bread particular, the Benghazi bakeries is free of potassium bromate.

#### Methodology:

Sixty different types of bread samples were randomly collected from 60 different bakeries in the city of Benghazi. The city of Benghazi was divided into 20 regions, and 60 samples were drawn out of bakeries, which is equivalent to three samples from each region. Three different samples of flour were also collected from the markets in Benghazi city, which is usually used for preparing dough and bread. The researchers prepared four samples of bread inside the Food and Water Analysis Laboratory (one of the Public Health Laboratories for Consultation and Research). The vanoise improver, which is commonly uses in all bakeries in Benghazi, was added to the first sample of bread, and the other three samples were kneaded by adding potassium bromate enhancer in different concentrations: 0.5 g / 1 kg, 0.25 g / kg, 0.1 g / kg. Four types of other improvers used in Benghazi (white flower made in Tunisia) (prima

made in Italy) (Vanoise made in Tunisia) (masterban made in Turkey) was also analyzed.

Laboratory Tests Used to Detect Potassium Bromate:

# ExperimentA:QualitativeDetermination (Black spot test)ForPresence of Bromate

Reagent: 0.5% potassium iodide in 2 MHCl. This was prepared by weighing 0.5g of potassium iodide in 100 mL of 2 MHCl, shaking gently to form a homogeneous solution. and was dispense into brown containers. Fresh reagent was used for testing bread samples directly. Principle: this is based on the reaction of bromate and iodide ions in an acid medium to produce triiodide. Procedure: 0.10 mL of the 0.5% fresh acidified potassium iodide solution was drops on the surface of the bread sample and examine for blackish spot after 2 minutes, which suggest the presence of bromate (Egan, H., Cox, H.E. and Pearson, D., 1981)

#### **Experiment B: Colorimetric quantitative method**

A 1.0 g of well-prepared sample was weight out from each bread sample in an electronic weighing balance, and transferred into a test tube.

10 ml of distilled water was add; the mixture was shacked well and allowed to stand for 20 minutes at  $28 \pm 10$  °C. A 5.0 ml volume was filtrated from the test tube. A 5.0 ml quantity of freshly prepared 0.5 % potassium iodide solution in 0.1N hydrochloric acid was add. Any color change was note. The presence of potassium bromate was indicate by change in color from light yellow to purple. The absorbance of the sample was taken at 620 nm in a UV visible spectrophotometer (GBC cinta 20). Absorbance of the sample was convert to concentration with reference to calibration curve previously constructed for potassium bromate using the pure sample. Values presented

are mean of five replicate determinations (Divid P, 1976).

#### **Result and Discussion:**

In this study, the researchers revealed whether the bread samples collected

from the 20 region of Benghazi city contained potassium bromate or not. Over the results mentioned in Table No. 1 to 4 for sixty sample, no samples of ready-made bread contained potassium bromate.

#### Table (1): Qualitative and Quantitative Results of Potassium Bromate Detection

in Different Bread Samples Colled	cted from Region No.	1 To Region No. 5
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Region Number	Bread samples	RESULT		
		*Qualitative method	Quantitative method mg/kg (ppm)	
	Bakery 1	negative	0.00 ppm	
1	Bakery 2	negative	0.00 ppm	
	Bakery 3	negative	0.00 ppm	
	Bakery 4	negative	0.00 ppm	
2	Bakery 5	negative	0.00 ppm	
	Bakery 6	negative	0.00 ppm	
	Bakery 7	negative	0.00 ppm	
3	Bakery 8	negative	0.00 ppm	
	Bakery 9	negative	0.00 ppm	
	Bakery 10	negative	0.00 ppm	
4	Bakery 11	negative	0.00 ppm	
	Bakery 12	negative	0.00 ppm	
	Bakery 13	negative	0.00 ppm	
5	Bakery 14	negative	0.00 ppm	
	Bakery 15	negative	0.00 ppm	

\*Negative means no black spot

### Table (2): Qualitative and quantitative results of potassium bromate detection indifferent bread samples collected from region No. 6 to region No. 10

Region Number	Bread Samples	Result	
		*Qualitative method	Quantitative method mg/kg (ppm)
	Bakery 16	negative	0.00 ppm

6	Bakery 17	negative	0.00 ppm
	Bakery 18	negative	0.00 ppm
	Bakery 19	negative	0.00 ppm
7	Bakery 20	negative	0.00 ppm
	Bakery 21	negative	0.00 ppm
	Bakery 22	negative	0.00 ppm
8	Bakery 23	negative	0.00 ppm
	Bakery 24	negative	0.00 ppm
	Bakery 25	negative	0.00 ppm
9	Bakery 26	negative	0.00 ppm
	Bakery 27	negative	0.00 ppm
	Bakery 28	negative	0.00 ppm
10	Bakery 29	negative	0.00 ppm
	Bakery 30	negative	0.00 ppm

\*Negative means no black spot

## Table (3): Qualitative and quantitative results of potassium bromate detection indifferent bread samples collected from region No. 11 to region No. 15

Region	Bread Samples	Result	
number		*Qualitative method	Quantitative method mg/kg (ppm)
11	Bakery 31	negative	0.00 ppm
	Bakery 32	negative	0.00 ppm
	Bakery 33	negative	0.00 ppm
	Bakery 34	negative	0.00 ppm
12	Bakery 35	negative	0.00 ppm
	Bakery 36	negative	0.00 ppm
	Bakery 37	negative	0.00 ppm
13	Bakery 38	negative	0.00 ppm
	Bakery 39	negative	0.00 ppm
	Bakery 40	negative	0.00 ppm

14	Bakery 41	negative	0.00 ppm
	Bakery 42	negative	0.00 ppm
	Bakery 43	negative	0.00 ppm
15	Bakery 44	negative	0.00 ppm
	Bakery 45	negative	0.00 ppm

\*Negative means no black spot

### Table (4): Qualitative and Quantitative Results of Potassium Bromate Detectionin Different Bread Samples Collected from Region No. 16 To Region No. 20

Region Number	Bread Samples	Result	
		*Qualitative method	Quantitative method mg/kg (ppm)
	Bakery 46	negative	0.00 ppm
16	Bakery 47	negative	0.00 ppm
	Bakery 48	negative	0.00 ppm
	Bakery 49	negative	0.00 ppm
17	Bakery 50	negative	0.00 ppm
	Bakery 51	negative	0.00 ppm
	Bakery 52	negative	0.00 ppm
18	Bakery 53	negative	0.00 ppm
	Bakery 54	negative	0.00 ppm
	Bakery 55	negative	0.00 ppm
19	Bakery 56	negative	0.00 ppm
	Bakery 57	negative	0.00 ppm
	Bakery 58	negative	0.00 ppm
20	Bakery 59	negative	0.00 ppm
	Bakery 60	negative	0.00 ppm

\*Negative means no black spot

To prove the accuracy of the laboratory experiments for the detection of potassium bromate, four samples of bread were prepared inside the laboratory, the vanoise improver was add to one sample, and potassium bromate was added to the rest of samples with different concentrations as shown in Table 5.

Number	Lab Bread Samples	Result	
		*Qualitative Method	**Quantitative method mg/kg (ppm)
1	Bread made by Vanoise improver	negative	0.00 ppm
2	Bread made by adding <b>Potassium</b> <b>bromate</b> at 0.5g/kg	positive	positive
3	Bread made by adding <b>Potassium</b> <b>bromate</b> at 0.25g/kg	positive	positive
4	Bread made by adding <b>Potassium</b> <b>bromate</b> at 0.1g/kg	positive	positive
*Negativ	ve means no black spot	1 1	

### Table (5): Qualitative and Quantitative Results of Potassium Bromate Detection in Bread Prepared in the Laboratory at Different Concentrations

\*Negative means no black spot

\*\*Positive means purple color

In addition, the three different samples of raw flour were collected from different supermarkets, which were used to make bread inside the laboratory, it also underwent to

qualitative and quantitative experimental, and the results showed that all flour samples are free of potassium bromate, Table (6).

#### Table (6): Qualitative and Quantitative Results of Potassium Bromate Detection

in Flour Samples

Number	Flour Samples	Result		
		*Qualitative method	Quantitative Method, mg/kg (ppm)	
1	Flour	negative	0.00 ppm	
2	Flour	negative	0.00 ppm	
3	Flour	negative	0.00 ppm	

\*Negative means no black spot

By way of using the qualitative method, the first sample of bread which made by vanoise improver was given negative result as show in Fig 1. The other three samples of bread that made by adding Potassium bromate as improver (0.25g/kg, 0.5g/kg, 0.1g/ kg)



Fig, 1: Bread made by Vanoise improver

directly to bread given positive result as shown in Fig 2, 3, and 4 respectively, with the appearance of blackish spot after 2 minutes. Different gradations, evidence of potassium bromate in varying proportions.



Fig, 2: Bread made by adding Potassium bromate at 0.25g/kg



Fig, 3: Bread made by adding Potassium bromate at 0.5g/kg

To increase the accuracy of our results, the quantitative method described in the methodology was done, and the results were identical to the qualitative method. As it was colorless with the vanoise bread samples (0.001 ppm kBro3), and the gradient was intensely purple with the other three bread samples prepared with addition of potassium bromate in the concentration of 0.5g/kg, 0.25g/kg, and 0.1g/kg. The gradient in color was due to the difference in the concentration



Fig, 4: Bread made by adding Potassium bromate at 0.1g/kg

of potassium bromate added to the samples, (Fig. 5).

As shown in Fig 6, calibration curve of 5ppm, 10ppm and 20ppm KBro3 indicated gradient yellow color with potassium iodide depending on the concentration of bromate. The bread samples give no yellow color (colorless) with potassium iodide that mean no KBro3 added.

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Fig, 5: Change in color during colorimetric quantitative detection of Potassium bromate in laboratory bread with difference concentration 0.25g/kg, 0.5g/kg, 0.1g/kg (tube 1, 2 and 3) respectively, bread samples without KBro3 (tube 4)



### Fig, 6: Calibration curve of solutions Potassium bromate at difference concentration (5ppm, 10pmm, 20 ppm) with acidified potassium iodide

Among the study, the researchers enhanced the accuracy of the absence of potassium bromate by detecting all types of improvers (Vanoise, White flower, Prima, and Masterpan) that used in in Benghazi bakeries,

both quantitatively and qualitatively experimental was done, and all types of improvers were recorded as a negative result, Table (7).

Table (7): Qualitative and Quantitative Results of Potassium Bromate Detection in
Improvers Used in Benghazi Bakeries

Number	Improver Samples	Result		
		*Qualitative method	Quantitative method, mg/kg (ppm)	
1	Vanoise improver	Negative	0.00 ppm	
2	White flower improver	Negative	0.00 ppm	
3	Prima improver	Negative	0.00 ppm	
4	Masterpan improver	Negative	0.00 ppm	

\*Negative means no black spot

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Quantitiatively and qualitatively teste indicated that all 60 bread samples that we analyzed are free of potassium bromate, which is consistent with the Codex Alimentarius Committee, which announced the withdrawal of potassium bromate as an additive since 2012 (Fao et al., 2012). Although the potassium bromate has been banned in Libya since 2005 due to classified as a probable carcinogen, and moreover the Ministry of Economy and Trade confirmed in the year 2021 to ban the import of "potassium" bromate" and prevent owners of bakeries, sweets and pastry factories from using "potassium bromate" in addition to mill owners, as they are prohibited from adding it to flour production. ( Libya's Ministry of Economy ). However, a study has been done in the Tajoura area in the city of Tripoli in 2020 (Edriss and Issa, 2020) resherares indicated that high levels of potassium bromate have been shown (300 to 1333ppm) to be more than, the tolerable level set by the US Food and Drug Administration (FDA). Another study has been conducted in 2022 by the Food and Drug Control Center, Tripoli branch (https://fdcc.ly, 2022), on 360 bakeries in the city of Tripoli and the western and southern regions, and all the results of the samples were completly negative, devoid of potassium bromate, and these results denied the results of the Tajoura study in 2020 or that strict measures were already taken to prevent the use of potassium bromate in the western region, which made the results of the study in 2022 completely free of potassium bromate. Potassium bromate is known to be highly toxic and can threaten health when consumed regularly for long periods of time. Hence, it is necessary to continuously monitor and implement the ban on the use of potassium bromate in the bread industry in the western region of Libya.

#### **Conclusion:**

In our study, all samples were completely free of potassium bromate and this confirms that potassium bromate was not used in bakeries in Benghazi, Libya, which has been banned since 2005. This does not preclude routine laboratory testing to ensure that bakeries always adhere to safety guidelines. Otherwise, bread makers should be educated about the importance of using alternative flour improvers that are safer for health.

**Approval:** According to the international standards or the standards of the corresponding universities, the bakery approval was collected and archived by the researchers.

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**Competing interests:** The authors state that there are no competing interests.

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