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Determination and Degradation of Potassium Bromate Content in Dough and Bread Samples Due to the Presence of Metals

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Abstract

Potassium bromate (PB) is used in bread making as an agent of maturation; however, it is classified as a potential carcinogen. In the present study, a rapid, simple, precise and accurate testing method has been developed to determine the level of bromate ions in bread, which is based on a reaction of bromate ions with iodide ions in acidic medium to produce iodine (I_2). The absorbance of iodine (I_2) was measured at 352 nm, and bromate ions reacted with iodide during the first 3 minutes after initiation of the reaction. The proposed method has been successfully applied to the determination of bromate ions in commercial bread. In this work, we found that bromate ions alone degraded at about 400˚C, however, during bread making they degraded at 150˚C - 200˚C, this mightbe due to the presence of metals [Fe, Mg, Zn, Mn, Cu and Al] in flour which served as catalysts. In this study we found that the use of two grams (2 g) of PB per bag flour (60 kg) was safe.

Keywords

Potassium Bromate, Dough, Bread, Catalyst, Flame Atomic Absorption, Inductively Coupled Plasma Mass Spectrometry

1. Introduction

Bread has a historical importance in many western and eastern societies as a staple food in many countries of the world [1] [2]. In many cultures, and in the west and middle east during the 1950s, the importance of bread was

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not used only as food, but also as a currency instead of money to buy the necessities of life, this besides being a main contributor for families in regards to living and economy [3].

In the west bank, bread is one of the most commonly consumed foods in homes and restaurants. Predominant consumption occurs among the poor and youth, in which the individual consumes an average of 9 small loaves of bread daily.

Bread is made from a type of flour (e.g. wheat, corn or barley) and some of the basic ingredients include table salt, water, yeast, others flavors, and at least one flour improver [4] [5]. PB 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 [6].

It makes the bread stronger and more elastic, and also promotes big rises of bread [7]. The resulting bread tends to be strong and springy, and especially well-suited to commercial production [8]. The mechanism of bromate ions activity in dough is complex and not understood. Sullivan *et al*. suggested the mechanism involved the protein fraction of flour. Jorgensen and Balls thought the oxidant inhibited the action of the proteolytic enzymes. Baker *et al*. concluded that a material in gluten that was salt soluble reacted with oxidants [8]. Although many hypotheses have been proposed, the theory chemists agree upon is that bromate ions oxidize thiol groups to disulfide linkages, thus strengthening the protein network, then the increase in dough expansion capacity and improvement of the bread appearance [8] [9]. The presence of bromate ions in bread may lead to renal failure, anemia, respiratory depression, and cancer in humans [10]-[14].

The Food and Drug Administration (FDA) allows the use of PB up to a maximum level of 50 mg/kg of flour mass in bread. However, Japan permits the inclusion only up to 10 mg/kg of flour [15]. In California, a warning label is required when bromated flour is used. Currently in California, it is recognized that it is inappropriate to use PB in any product or production method, which can be formulated with residues below the level of 20 ppb (*i.e.* 0.020 mg/kg) in the finished product [16]. The Food and Agriculture Organization (FAO)/World Health Organization (WHO) joint committee's initial recommendation of acceptable level of 0 - 60 mg $KBrO_3$/kg flour was withdrawn because of long term toxicity and carcinogenicity studies (*in vitro* and *in vivo*), which had revealed the development of renal cell tumors in hamsters [17].

In this work, we report a very simple and sensitive method for direct determination of PB in bread and flour, which has been based on bromate ions oxidation of iodide to produce iodine (I_2).

2. Materials and Methods

The following reagents were used: hydrochloric acid (SDFCL), glycine (Riedel), potassium iodide (Frutarom), potassium bromate (Frutarom) and distilled water. The following apparatus were used: UV spectrophotometer, pH meter, hot plate, furnace and inert gas (N_2). Flour and bread samples were purchased from the markets of west bank. A total of twenty one different sample of bread were used in the study.

2.1. Preparation of Standard Solutions

Three runs were needed for each sample. Standard solutions of bromate were prepared ranging from 1 ppm to 10 ppm from the stock solution of $KBrO_3$ were transferred into a 10 ml volumetric flask. Then, 1.0 ml of buffer solution was added. The solution was diluted to 9.0 ml with distilled water and 1.0 ml of a potassium iodide solution was added. A stopwatch was started just after the addition of iodide solution. A portion of solution was transferred into 1-cm quartz cell to measure the absorbance at 352 nm during the first minutes after initiation of reaction. Results were used to plot the calibration curve and calculate the equation of the linear regression.

2.2. Preparation of Samples with Known Amounts $KBrO_3$

Bread and dough was prepared using the following recipe: flour (100 g), yeast (1 g) and water (80 g). Seven bread samples were prepared with different amounts (0, 50, 100, 150, 200, 250, 300 ppm) of potassium bromate. Ingredients were mixed in the beaker by using a glass rod for 2 min. Then, the dough was fermented for 20 min. Finally for the bread, the dough was baked at 270˚C for 15 min.

2.3. Sample Treatment

A sample of 10 g of dough was cut and triturated into 100 mL of distilled water with a magnetic stirrer and then filtered. A measured volume of the filtrate solution (5 mL) was transferred into a 10 ml flask, 1.0 mL of buffer solution was added to the filtrate. Then, the solution was diluted to 9.0 mL with distilled water and 1.0 mL of an iodide solution was added. The absorbance was measured after mixing for each sample (3 runs for each sample). The unknown concentration of bromate was calculated from the linear regression curve obtained from the standard solutions of bromate.

2.4. Effect of Temperature on Potassium Bromate

The effect of temperature on potassium bromate was investigated from 25˚C to 400˚C the temperature in which all potassium bromate decomposed. 0.5 g of potassium bromate was placed in a crucible, and then transferred the crucible to the furnace at the desired temperature for 15 min. After 15 min, 100 ppm of potassium bromate were prepared for each sample in distilled water and in flour, then the absorbance of iodine (I_2) was measured.

Analysis flour sample by inductively coupled plasma-mass spectrometry ICP-MS.

Five grams of flour were digested with nitric acid at room temperature and analyzed by ICP-MS for detecting the metals present.

3. Results and Discussion

3.1. Determination of Optimum Conditions

To establish the optimal conditions for the bromate-iodide reaction, series of experiments were carried out. All parameters were studied in regards to the effect of iodine. This was accomplished by altering each variable in turn, while keeping other variables constant.

Bromate ions react with iodide in acidic media to produce iodine according to this equation:

$$\mathrm{BrO}^-_{3(aq)} + 6\mathrm{I}^-{}_{(aq)} + 6\mathrm{H}^+{}_{(aq)} \rightarrow 3\mathrm{I}_{2(\mathrm{aq})} + 3\mathrm{H}_2\mathrm{O}_{(\mathrm{l})} + \mathrm{Br}^-{}_{(\mathrm{aq})}$$

The reaction could be monitored spectrophotometrically by measuring the absorbance of the solution at 352 nm, which is proportional to I_2 concentration. From the equation, iodine production depends on the pH and reagent concentrations (potassium iodide). So it was determined that the suitable optimal condition for producing large amounts of iodine and giving high absorbance.

3.2. Effect of pH

The effect of the pH on the reaction of bromate ions was studied. Three runs were used for each sample. All conditions were the same for the three runs, except the pH, which was different for each sample. The results are shown in **Figure 1**.

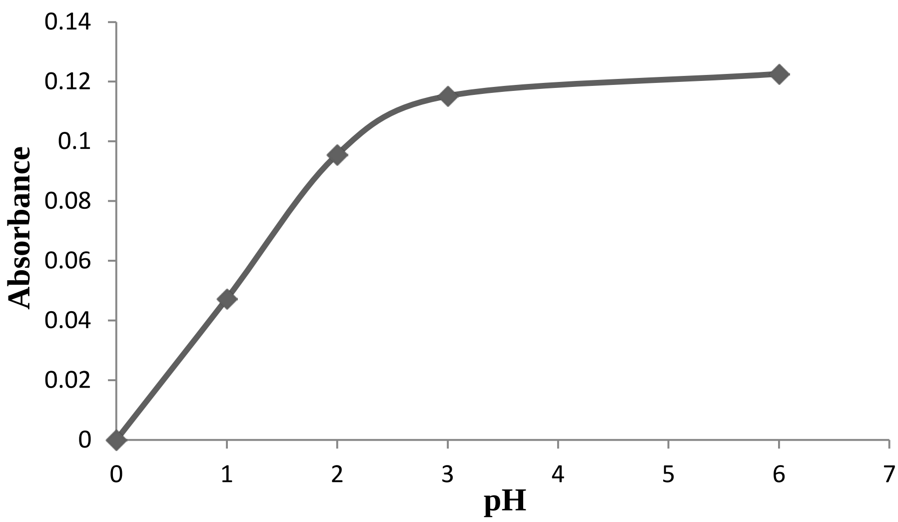

Figure 1. Effect of pH in the range of 4.0 - 1.0 on the reaction.

As the figure shows, investigated anion (bromate ions) did not react with iodide in the range of pH from 2.0 to 4.0 during the first 4 min after mixing, even when the concentration of bromate ions was 100-fold in excess over 5 ppm. Also as the obvious figure shows, bromate ions reacted with iodide in the range of pH from 1.0 - 1.5 during the first 4 min after mixing, but the reaction rate increased at pH values lower than 1.5. Therefore, a pH of 1.0 was selected as the optimum pH for the reaction and the absorbance change during the first 4 min after mixing was proportional to the bromate ions concentration.

3.3. Effect of Potassium Iodide Concentration

The effect of the iodide concentration on the rate of the reactions was investigated at a concentration of 5 ppm of bromate ions and by varying the concentration of iodide in the range of 0.025 - 0.6 M. The results are shown in **Figure 2** at pH 1 (optimal pH).

As **Figure 2** shows, at pH 1, the absorbance during the first 4 min after initiation of a reaction for bromate ions increased (linear) upon increasing the iodide concentration up to 0.3 M, and remained nearly constant at higher concentrations (zero order and constant rate). Therefore, the maximum absorbance during the first 4 min was obtained with iodide concentration at 0.1 M to suppress air oxidation.

3.4. Optimization the Time of Reaction

The suitable time to complete the reaction was studied for 5 ppm of bromate ions. The absorbance of iodine I_2 was measured at pH 1 and 0.1 M iodide concentration for 15 min. The results are shown in **Figure 3**.

As **Figure 3** shows, the complete reaction required 3 min. Therefore, the absorbance of iodine (I_2) was measured during the first 3 min and the optimum conditions were applied in further experiments.

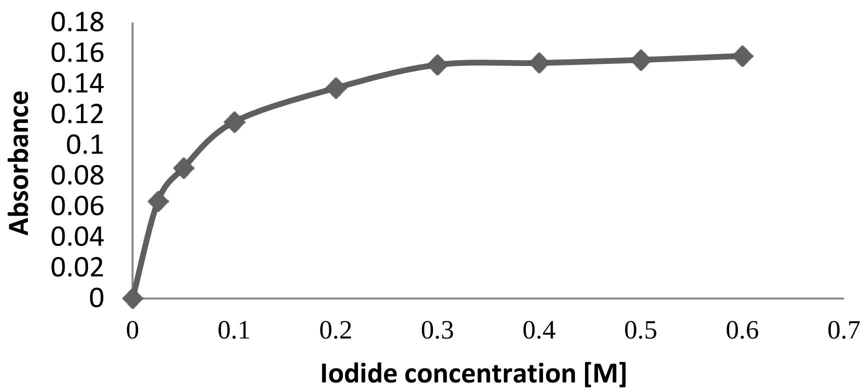

Figure2. Effect of iodide on the reaction at pH 1.

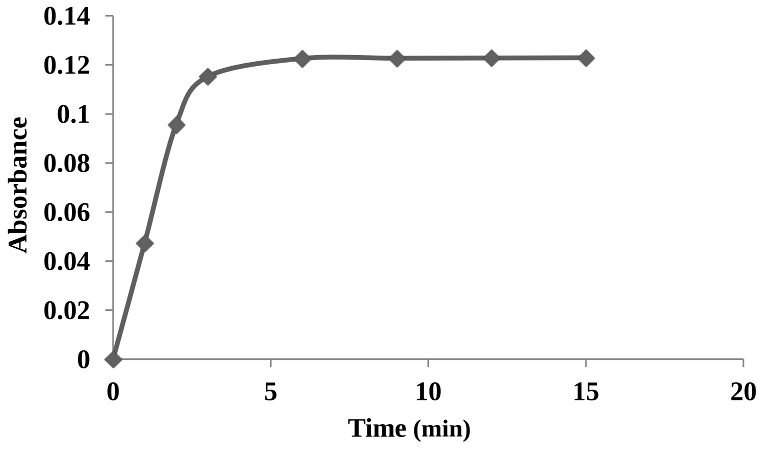

Figure3. Optimization the time of reaction at pH 1 and 0.1 M KI.

3.5. Calibration Curve

Calibration graphs for the determination of bromate ions in distilled water, dough and bread were obtained under the optimum conditions using different calibration curves.

3.6. Effect of Temperature on PB

The effect of temperature on bromate ions was studied in the range from 50˚C to 400˚C in which all potassium bromate ions decomposed. The effect of temperature was studied at 50 ppm of bromate solution for each sample. The results are shown in **Figure 4** (the absorbance measured at pH 1 and iodide concentration 0.1 M).

As **Figure 4** shows, the absorbance of iodine (I_2) decreased upon increasing the temperature during the first 3 min after mixing the bromate ions. The absorbance was in the range from 350˚C - 400˚C ≈ zero, this meaning that the bromate ions decomposes and converts to KBr and O_2 from heating as in equation:

$$2KBrO_3 \rightarrow 2KBr + 3O_2$$

Bromate decomposes in distilled water at (350˚C - 400˚C) but in bread decomposes within the range of 150˚C - 250˚C. The decomposition of bromate ions in bread at low temperatures may be due to the presence of metal ions in flour, which acts as a catalyst is clear in **Table 1**.

Table 1. Metal ions in flour analyzed by inductively coupled plasma mass spectrometry.

Element	Molecular Mass	Net Intens. Mean	Conc. Mean (ppb)	Conc. (ppm)
Ag	107	40.33	0.06	0.01
Al	27	20,300.24	13.25	2.65
Ba^{-1}	138	5402.54	3.54	0.71
Be	9	0.00	0.00	0.00
Bi	209	38.00	0.03	0.01
Ca	43	4455.74	726.41	145.28
Cd	111	5.0	0.03	0.01
Co	59	59.33	0.04	0.01
Cr	52	11,372.42	7.51	1.50
Cs	133	8.33	0.01	0.00
Cu	63	5085.44	7.15	1.48
Fe	57	2802.85	74.15	14.83
Ga	69	260.34	0.19	0.04
In	115	12.37	0.01	0.00
K	39	35,388,241.17	5915.11	1183.02
Li	7	−5.67	−0.01	0.00
Mg	24	709,924.12	785.07	157.01
Mn	55	42,062.33	22.40	4.48
Mo	98	1075.54	1.43	0.29
Na	23	241,316.04	106.55	21.31
Ni	60	643.70	2.19	0.44
Pb	208	52.67	0.06	0.01
Rb	85	6892.62	3.27	0.65
Sr	88	12,075.60	4.47	0.89
V	51	−38.34	−0.02	0.00
Zn	66	6107.83	31.45	6.29

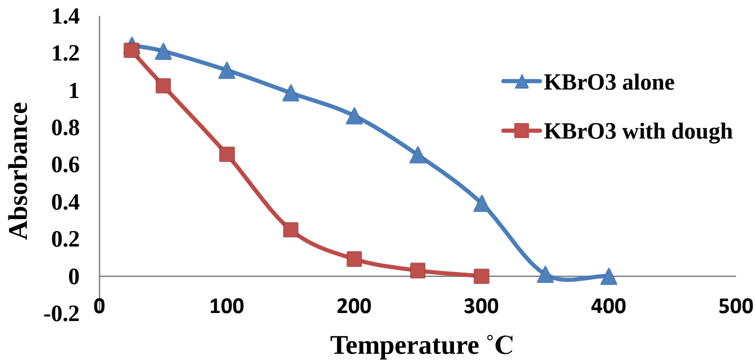

Figure 4. Effect of the temperature on the PB.

3.7. ICP-MS

Looking at the results in **Table 1**, several metals are shown: Fe, Mg, Zn, Mn, Cu and Al. All of these metals have a big role in the degradation and oxidation of PB. It is possible that PB reacted with those metal ions and caused Oxidation-Reduction reactions (electron transfer). There was a chelating agent, due to the presence of Mn as a catalyst, which reduces the presence of PB action in bread making,

4. Conclusion

The present work describes a simple, rapid and validated method for determining bromate ions. This method is based on bromate's reaction with iodide ions in an acidic medium to produce iodine (I_2). The determined method can be recommended for the routine control of bromate ions in bread bakeries. This method can be used as an alternative repetitive method for laboratories, not equipped with expensive materials necessary for the procedure. Potassium bromate in bakeries might be allowed at a certain ratio and up to 2 g per bag (60 Kg).

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