

NOTE

Analysis of Potassium Bromate in Flour, Dough, and Bread

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Potassium bromate (bromate) has been used as a dough conditioner for at least 60 years. It improves dough processing properties, internal crumb quality, and loaf volume in concentrations from a few to 75 parts per million (ppm), the highest concentration permitted by law. The optimum usage level depends upon the type of baking method. The mechanism by which bromate acts in dough is complex and not well understood. The current situation is aggravated by the fact that good analytical methods are lacking for its detection and measurement in bread dough systems. Of those currently available, Cunningham et al (1956) and Thewlis (1977) are based upon iodometric titrations (AACC 1982, method 48-42), and Hlynka et al (1953) is based on iodometric spectrometry; all of these lack selectivity and sensitivity. Furthermore, this chemical oxidant is suspected of being a carcinogen.

A reliable method for the analysis of bromate in flour, dough, and bread is important for determining how it is utilized in different baking systems. Such information would be useful in the development of a bromate substitute, as well as improving the understanding of the oxidation mechanism.

In 1988, De Stefanis et al reported a novel method based on oxidation of a dye by bromate. At that time, the method was used for screening metal ions that exhibited bromate catalytic

properties. Research in this area was expanded to develop a quantitative procedure for use in flour, dough, and bread.

This note describes the development and application of that procedure.

MATERIALS AND METHODS

Flour

Commercially milled flour was unbleached, unmalted, and untreated. The flour contained 11.9% protein, 10.3% moisture, and 0.43% ash. Flour was treated with 0-75 ppm potassium bromate (J. T. Baker) and was analyzed for bromate.

Breadmaking Method

Bread was made by the "no time" baking method. The formulation consisted of 2% salt, 4% dextrose, 2% shortening, and 3% compressed yeast. Aliquots of a bromate solution were added to flour at the beginning of dough mixing. Depending on the type of experiment, aliquots were added either to a dough or a bread crumb suspension.

Instrumentation

Absorbances of the reaction solutions were measured at 625 nm using a Spectronic 21 spectrophotometer (Bausch & Lomb, Rochester, NY).

Preparation of Reagents

Zinc sulfate solution was prepared as 10% (w/v) $ZnSO_4 \cdot 7H_2O$ (Fisher Scientific, Fairlawn, NJ).

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Citric acid solution was prepared as 5% (w/v) $C_6H_8O_7 \cdot H_2O$, adjusted to pH 3.0–3.10 (J. T. Baker, Phillipsburg, NJ).

Dye solution was a 0.05% (w/v) solution of 4,4'-diaminodiphenylamine sulfate (ICN Pharmaceuticals, Life Sciences Group, Plainview, NY). It was prepared as follows. Dye (0.05 g) was transferred to a 100-ml volumetric flask along with 50 ml of H_3PO_4 solution (0.1N). After shaking for 10 min, the pH of the solution was adjusted to 3.00–3.10 with NaOH (1N), diluted to volume with deionized water, and mixed. The solution was allowed to stand for 10 min before being filtered through Whatman no. 1 paper. The filtrate was transferred to an amber bottle. The dye solution was prepared fresh daily.

A vanadium-containing solution was made up at 0.005% (w/v) using vanadyl acetate (City Chemical Corp., New York) or ammonium vanadate (MCB, E. Rutherford, NJ). Vanadium compound (0.25 g) was transferred to a 500-ml volumetric flask along with 250 ml of 0.1N H_3PO_4 solution. After shaking for 10 min, the pH was adjusted to 3.00–3.10 with 1N NaOH, diluted to volume with deionized water, and mixed. The solution was allowed to stand for 10 min before being filtered through Whatman no. 1 paper. The filtrate was transferred to an amber bottle. The solution was prepared weekly.

Development of Method for Bromate Determination

The principle of the method is based upon the bromate oxidation of the dye, which changes the color of the solution from a faint purple to blue. In developing the method, variables such as pH, temperature, catalyst and dye concentrations, ratio of dye to catalyst, and reaction time were taken into consideration. Simplicity was the goal in developing the extraction procedure and extract purification. Briefly, bromate oxidizes the dye at an exceedingly slow rate at 23–25°C. The oxidation reaction can be accelerated and controlled by using the vanadium ion, which acts as a catalyst (De Stefanis et al 1988). Under the conditions of the method, the reaction reaches maximum color at the end of 45 min (pH 3.00–3.10 and 23–25°C.). A long reaction time was chosen purposely to ensure control and reproducibility of data. The absorbance at 625 nm increased in proportion to bromate concentration.

The procedure encompasses three steps: extraction, purification of extract, and spectrometry. The proportions suggested for the analysis of bromate in typical bread doughs appear below. Correct sample weights must be established by the analyst.

Unbromated and bromated samples (flour, dough, and bread crumb) were handled in the same manner throughout the entire procedure. The unbromated extract (no bromate added) was used to set the spectrophotometer to zero. Substrate samples containing bromate were measured against unbromated samples.

Extraction. Portions of test dough (50.0 g) plus 100 ml of deionized water were transferred to a blender (Waring) and mixed for 2 min at an intermediate speed. At the end of mixing, one to two drops of 1-octanol were added to the slurry, which was mixed, transferred to a centrifuge bottle (200–250 ml), and centrifuged at 2,000 rpm for 5 min. The supernatant was passed through glass wool, resulting in crude extract.

Purification of the extract. An 85-ml portion of the crude extract was combined with 10 ml of $ZnSO_4$ (10%) and 5 ml of NaOH solution (1N) in a 100-ml glass-stoppered graduated cylinder and mixed (pH 6.2–6.50). The mixture was allowed to stand for 5–10

min before centrifugation at 2,000 rpm for 10 min. The obtained supernatant was filtered through Whatman no. 1 paper.

Spectrometry. A 25-ml aliquot of filtrate was pipetted into a 50-ml glass-stoppered graduated cylinder; 1 ml of 5% citric acid solution was added, and the cylinder was stoppered and mixed. Two milliliters of the dye solution was pipetted into the cylinder and mixed; then 2 ml of either vanadyl acetate or ammonium vanadate solution was pipetted into the cylinder and mixed. The reaction was timed, and then the solution was diluted to 50 ml with deionized water. A final mixing was given to the entire mixture. The reaction was conducted at pH 3.00–3.10 and 23–25°C. At the end of 45 min, the instrument was set to zero with the unbromated dough extract. Bromated dough extracts were measured at 625 nm. Bromated and unbromated dough extracts were treated in the same manner throughout the entire procedure. It was found that the sensitivity of the procedure could be increased by using 20 ml of the dough extract, 2 ml of the dye solution, and 3 ml of the vanadyl acetate solution, the mixture diluted to 30 ml with deionized water. The latter procedure was effective in detecting 1 ppm bromate in dough.

The developed procedure was used successfully for the analysis of bromate in flour, flour brew, water brew, sponge, dough, and bread crumb.

RESULTS AND DISCUSSION

Differentiation Between Bromate and Bromide

The general consensus in cereal chemistry is that after exerting its oxidative action, potassium bromate is converted to potassium bromide. The described method is selective for bromate (Table I).

Recovery of Bromate from Dough

Known levels of bromate (25, 50, and 75 ppm) were added to flour at the beginning of dough mixing. In another case, corresponding levels were added to the unbromated dough extract at the purification step of the procedure. From this point onward, the procedure was the same as described. This approach was

TABLE II
Recovery of Potassium Bromate from Fully Developed Doughs

Bromate Added to Dough (ppm)	Absorbance ^a (625 nm)	
	Bromate Added at Start of Mixing	Dough Extract "Spiked" with Bromate ^b
25	0.273	0.288
50	0.545	0.558
75	0.762	0.773

^a Mean of triplicate extractions (absorbance standard deviation of ± 0.005).

^b Bromate added to unbromated dough extract at the purification step of the procedure.

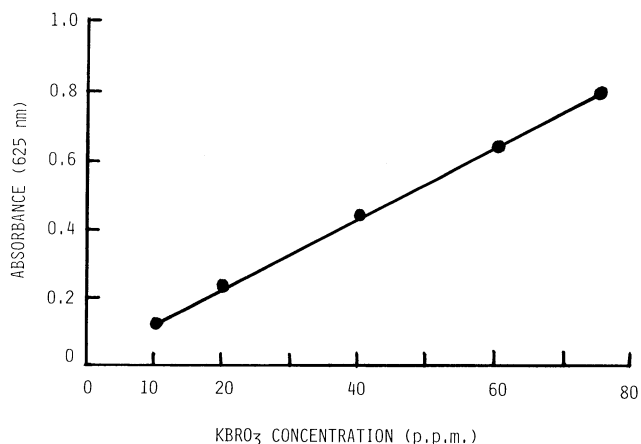


Fig. 1. Typical pattern of doughs containing increasing concentrations of $KBrO_3$, according to the described method.

TABLE I

Selective Reaction Between Dye and Potassium Bromate

Variable	Absorbance at 625 nm ^{a,b}	
	Mean	Standard Deviation
Reagents	0.140	± 0.005
Reagents + potassium bromide ^c	0.152	± 0.006
Reagents + potassium bromate ^c	2.0	± 0.006

^a Instruments set to zero with deionized water.

^b Means of triplicate analyses.

^c Absorbances measured after 45 min at 23–25°C, pH 3.00–3.10.

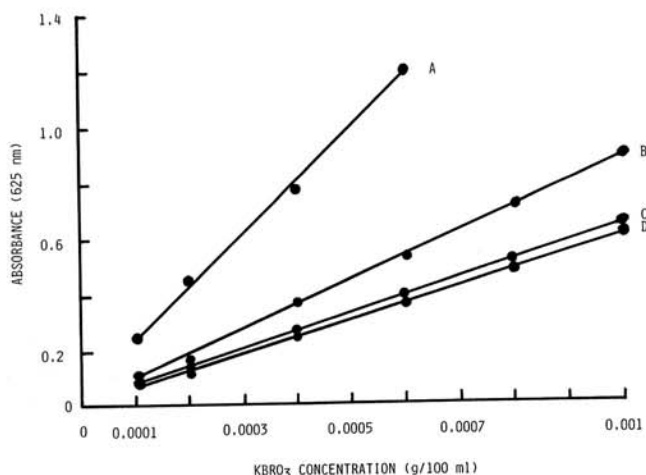


Fig. 2. Typical graphs of pure aqueous solutions (A) and of suspensions of flour (B), dough (C), and bread crumb (D) containing increasing concentrations of KBrO_3 . Flour (10.0 g), dough (18.0 g), and bread crumb (18.0 g) were spiked with 0.0001–0.001 g of KBrO_3 per 100 ml of water at the extraction step of the procedure. Bromated and unbromated substrates were handled in the same manner according to the described procedure. Maximum color development was measured after 45 min at 23–25°C.

employed to determine whether any bromate would be lost at the extraction step. Results of bromate recovery from dough are shown in Table II.

Application of Procedure to Doughs

Various bromate concentrations (10–75 ppm) were added to flour at the beginning of mixing. Doughs were mixed to optimum development. A portion of dough (50 g) was analyzed for bromate by the described procedure. Figure 1 illustrates a typical response of absorbance to increasing bromate concentration.

Analysis of Bromate in Flour, Dough, and Bread

Unbromated flour, dough, and bread crumb were “spiked” with known amounts of bromate (10–75 ppm) at the beginning of the extraction step of the procedure. Unbromated and bromated samples were handled in a similar manner for the remainder of the procedure. Figure 2 illustrates typical responses for the different substrates. The procedure was obviously more sensitive to pure solutions than to flour-containing substrates. Flour and yeast components suppressed the sensitivity of the procedure.

Reaction Between Dye and Other Oxidants

The procedure described herein was developed specifically for potassium bromate. A separate experiment was conducted to determine whether other oxidants generally used in baking also reacted with the dye or whether the reaction between bromate

TABLE III
Reaction Between Dye and Other Oxidants

Oxidant ^a	Absorbance ^b (625 nm)	
	Dye ^c	Dye + Catalyst ^d
Azodicarbonamide	0.85	0.75
Potassium iodate	0.70	0.60
Potassium bromate	0.13	1.00
Potassium bromide	0.01	0.02
Ascorbic acid	0	0
Cupric sulfate	0.01	0.005
Calcium peroxide	0.01	0.005
Benzoyl peroxide	1.70	1.00

^a0.01% (50 ml used for the analysis).

^bAbsorbances measured after 1 hr at 23–25°C (mean of triplicate analyses).

^c4,4'-Diaminodiphenylamine sulfate dye only (no catalyst).

^dDye + catalyst (vanadyl acetate).

and the dye was unique. This experiment was conducted with pure aqueous solutions, with and without the catalyst (vanadium) (Table III). Oxidants such as benzoyl peroxide, azodicarbonamide (ADA), and potassium iodate reacted positively with the dye. This reaction occurred rapidly in the absence of the catalyst. Without vanadium, the reaction was fastest with ADA and faster with iodate than with benzoyl peroxide. Bromate did not react with the dye effectively unless the catalyst (vanadium) was present. The reaction profile obtained with the dye follows the same pattern observed in actual baking, i.e., ADA reacts faster than iodate, and bromate is the slowest.

CONCLUSIONS

The developed method for bromate worked well on pure aqueous solutions and on flour, dough, and bread substrates. Currently, it is being used to follow bromate consumption in different types of baking systems. The information generated by these experiments would be valuable in developing effective replacers for bromate, as well as in improving our understanding of the oxidation mechanism.

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