

The Effect of Metal Ions on Bromate Oxidation During Breadmaking¹

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ABSTRACT

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A colorimetric procedure was developed to identify metal ions that accelerate the action of KBrO_3 . Absorbances correlated well with the baking results. This study investigated whether metal ions generally encountered during breadmaking influence bromate oxidation. Vanadium, copper, iron (Fe^{2+}), silver, and mercury exhibited a positive effect on bromate. No further research was conducted with either silver or mercury because of their adverse action on the amylases, proteins, and yeast. Bromate oxidation was accelerated in the following order: vanadium > copper > Fe^{2+} . Whereas the rate of acceleration was in proportion to the concentration of either vanadyl acetate or cupric sulfate (0-50 ppm),

ferrous sulfate was effective to 100-150 ppm. Above 150 ppm, loaf quality declined in relation to concentration. Iron in the ferrous state was a more effective KBrO_3 accelerator than ferric iron. Subsequent research showed, unequivocally, that copper (alone) operated as an oxidant similar to KBrO_3 . In contrast, vanadium and ferrous ions behaved as bromate catalysts. The action of the catalytic ion was on KBrO_3 and not on KBr . The catalytic property of vanadium was also tested on other oxidants, such as ascorbic acid, potassium iodate (KIO_3), and azodicarbonamide. Although it had no effect on either ascorbic acid or KIO_3 , vanadium also catalyzed the action of azodicarbonamide.

When potassium bromate (KBrO_3) is added to bread dough at the optimum level, both dough processing characteristics and loaf volume are improved. How KBrO_3 accomplishes these changes in baking has been a subject of intense investigation for the past 60 years. Sullivan et al (1940) suggested that the oxidation mechanism involves the protein fraction of flour. Jorgensen (1936) and Balls and Hale (1936) thought that the oxidant inhibits the action of the proteolytic enzymes. By means of flour fractionation and reconstitution techniques, Finney (1943) demonstrated that the water-soluble and gluten fractions of wheat flour are involved in the bromate action. Baker et al (1942) also concluded that a material in gluten that was salt soluble reacts with the oxidants. Hosney et al (1972) proceeded further with their investigation and identified phosphoric acid as one of the factors in flour involved in the bromate action.

Although many hypotheses, at times conflicting, have been proposed for the oxidation mechanism, one most cereal chemists agree upon is that KBrO_3 oxidizes the protein sulfhydryls to disulfides, promoting inter- and intramolecular cross-linking between peptide chains.

For the past several years, our laboratory has been conducting research in "no-time" baking in ambient and subambient (frozen dough) dough-mixing environments. Results, to date, suggest that the KBrO_3 mechanism is much more complex than simple oxidation of protein sulfhydryls to disulfides. Metal ions were found to influence the bromate response in baking.

Research on the effect of metal ions on bromate oxidation in breadmaking is limited. Jorgensen (1945) reported that CuSO_4 was added to spoiled flours for improvement as far back as 1860. Hlynka (1957) studied the effect of metal ions on dough relaxation, but his efforts were concentrated mainly on the effect of complexing agents in dough. Finney et al (1949) studied the effect of metal ions on gas production and loaf volume. Their work focused mainly on the effect of cadmium on yeast fermentation.

Bushuk and Hlynka (1960) studied the effect of different chemicals on the bromate reaction in dough by the amperometric titration method. Their study was not extended to breadmaking.

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This research was undertaken to determine the effect of metal ions on the bromate response (and that of other oxidants) in breadmaking for the purpose of learning more about the oxidation mechanism.

MATERIALS AND METHODS

The following metallic salts (reagent grade) were tested for their catalytic property on bromate: NaCl, KCl, CaSO₄, MgSO₄, MnSO₄, FeSO₄, FeCl₃, ZnSO₄, CuSO₄, Al₂(SO₄)₃, Ni(NO₃)₂·6H₂O, CoCl₂·6H₂O, Pb(NO₃)₂, SnCl₄·5H₂O, BaCl₂·2H₂O, Se (metal), Se (HNO₃ solubilized), (NH₄)₆Mo₇O₂₄·4H₂O, VC₂H₃O₂, AgNO₃, and Hg(C₂H₃O₂)₂. These salts were obtained either from J. T. Baker Chemicals or Fisher Scientific Co.

4,4'-Diaminodiphenylamine sulfate (DDA) was used as the reagent for screening metal ions (K&K, ICN Pharmaceuticals, Inc; Lifescience group, Plainview, NY). Typical patent bread flour (commercially milled) used for all baking experiments had a moisture content of 13.4%, protein of 13.8%, and ash of 0.50%. Potassium bromate (KBrO₃) (reagent grade) was obtained from J. T. Baker Co.

The following formulation was used for breadmaking: flour, 100.0%; yeast, 2.5% (ambient dough mixing) or 5.0% (subambient dough mixing); shortening, 2.0%; salt, 1.8%; dextrose, 1.0%; water, optimum (ambient dough mixing) or 4.0% less than optimum (subambient dough mixing).

All experiments were conducted with 1-lb loaves of bread.

Bread was made by the no-time baking method, according to the following procedure: flour, other ingredients, and additives were transferred to the bowl of a Hobart 120 mixer. Presuspended yeast was added to the dry ingredients and mixed for 1 min at slow speed. Salt and dextrose, predissolved in the remainder of the absorption water, was transferred to the mixer. The dough was mixed to optimum development, rested for 5–10 min, molded, panned, allowed to proof (108–110° F, 83% rh) to 1-in. above the pan, then baked at 425° F for 20 min. Bread was cooled to ambient temperature for 1 hr, followed by loaf volume measurement (rapeseed displacement). Loaf quality was evaluated 24 hr later.

The DDA reagent was prepared fresh daily by shaking 0.05 g of DDA in 70–80 ml of 0.01 M sodium acetate buffer (pH 5.00) for 15 min in an amber volumetric flask, diluted to the 100 ml mark with the buffer, mixed and filtered through Whatman No. 4 filter paper. The clear filtrate was stored in an amber bottle.

Different metallic salts were tested for their catalytic activity as follows: 1 ml each of sodium acetate buffer (0.1M, pH 5.00), aqueous oxidant solution (100 ppm), and aqueous metal solution (2,000 or 100 ppm, as indicated) (added in this order) were transferred to a 10-ml volumetric flask and mixed. One milliliter of

the DDA reagent was added, mixed, and the reaction time was recorded. Each test solution was diluted to 10 ml with H₂O and mixed. After exactly 15 min of reaction time, each test solution was measured at 625 nm. Under these conditions, KBrO₃ alone exhibited limited action, whereas a metal ion with catalytic activity increased the KBrO₃ oxidation of DDA, changing the pale purple solution to a greenish blue. The extent of catalysis was directly proportional to the absorbance of the test solution.

Each metal salt was first tested at 2,000 ppm. If that proved positive, the analysis was repeated at 100 ppm. If still positive, then it was tested in breadmaking.

Other bread oxidants, such as ascorbic acid (AA) (Hoffman La Roche), potassium iodate (KIO₃) (J. T. Baker), and azodi-carbonamide (ADA) (Maturox; Pennwalt Corporation) were also evaluated.

RESULTS AND DISCUSSION

The no-time baking method and subambient dough mixing (63–65° F) were chosen as conditions for this research because the oxidation response is much more observable than in other processes. The effect of KBrO₃ concentration on bread loaf specific volume is illustrated in Figure 1. Volume response was linear with KBrO₃ concentration.

Throughout this paper, loaf specific volume is used as the criterion for the oxidation response. One needs to recognize, however, that volume is not due to a single factor, but the result of many factors. Testing of all metals at varied concentrations would have been a formidable undertaking. Therefore, a rapid screening test was developed that met the following objectives: it identified ions with potential catalytic activity, and the catalytic activity obtained analytically correlated with baking.

The screening procedure measures the rate of KBrO₃ oxidation of DDA (dye) under standardized conditions. KBrO₃ alone exerts little oxidative effect on the dye. However, when catalytic metal ions are present, the oxidation of DDA is accelerated. Similar analytical approaches, but in reverse, were adopted by Córdoba et al (1985) for the analysis of vanadium in petroleum products and by Zhelyazkova et al (1972) in beans. Application of the screening procedure is illustrated in Table I. The catalytic effect of vanadium is also demonstrated in baking (Fig. 2).

Metal ions generally encountered during breadmaking, whether derived from flour or ingredients, were tested for their KBrO₃ catalytic potential by colorimetry (Table II). Initial results indicated the effect to be highest with vanadium, followed by copper and iron (Fe²⁺). Silver and mercury also exhibited positive properties, but no further testing was conducted with these ions because of their tendency to inactivate the amylases, sulfhydryl-blocking properties (Sullivan et al 1961), and toxicity to yeast.

Metallic salts having either catalytic or noncatalytic properties on KBrO₃ (Table II) were selected for testing in baking. Table III demonstrates that the pattern obtained by colorimetry paralleled the baking results. Na, K, Ca, Fe³⁺, and Zn ions exhibited no catalytic activity on bromate, whereas vanadium, copper, and ferrous ions had a positive effect. Both colorimetric and baking data showed catalysis to be highest with vanadium, followed by copper and iron (Fe²⁺). The ferrous (Fe²⁺) form exerted a greater catalytic effect on KBrO₃ than ferric (Fe³⁺).

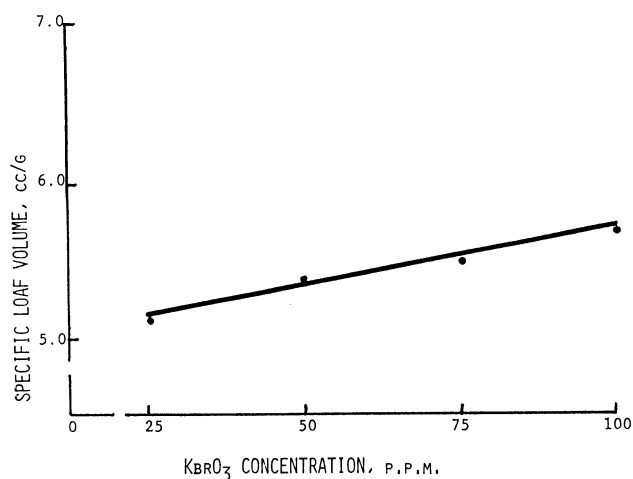


Fig. 1. Effect of KBrO₃ concentration on bread loaf specific volume. Flour was treated with 25, 50, 75, and 100 ppm bromate. Doughs were mixed at 63–65° F. Breads were made by the no-time baking method.

TABLE I
Catalytic Effect of the Vanadium Ion
on KBrO₃ Oxidation of DDA^a by Colorimetry

KBrO ₃ Concentration (ppm)	Vanadyl Acetate Concentration (ppm)	Absorbance ^b	
		(625 nm)	Standard Deviation
100	0	0.04	0.01
0	10	0.12	0.02
100	10	1.20	0.09

^a4,4'-Diaminodiphenylamine sulfate.

^bReaction time of 15 min at pH 5.00. Mean of triplicate analysis.

It was stated before that a no-time dough mixed at subambient temperatures (63–65° F) provides a good model for studying the catalytic properties of metal ions in baking. The effect of vanadium (vanadyl acetate) concentration on loaf volume is illustrated in Figure 3. Volume response was directly correlated with the concentration of vanadyl acetate (0–50 ppm). It should be noted that at 30 ppm, the dough-mixing requirements had to be reduced by 15%, and at 50 ppm by 30%, to maintain optimum bread quality.

The effect of FeSO₄ (bakery grade) concentration on KBrO₃ in baking is illustrated in Figure 4. Loaf volume increased to 100–150 ppm. Above 150 ppm, bread quality progressively deteriorated in relation to concentration.

Ferrous sulfate (bakery grade) is frequently used as a source of iron in flour enrichment. When added to bromated flour, the following precautions should be taken into consideration in breadmaking: 1) Because of its catalytic action on KBrO₃, less bromate is required to achieve the same level of oxidation. 2) Care should be taken not to exceed 150 ppm of FeSO₄. Bread quality progressively declines above this concentration. 3) FeSO₄ and KBrO₃ should be in balance with one another to prevent overoxidation.

Specific loaf volume also increased in proportion to copper

TABLE II
Effect of Different Metal Ions on Bromate Oxidation

Metal Ion	Metallic Salt ^a	Absorbance ^b (625 nm)	Catalytic Activity
KBrO ₃ (only)	...	0.030	...
Na	NaCl	0.055	...
K	KCl	0.050	...
Ca	CaSO ₄	0.060	...
Mg	MgSO ₄	0.085	...
Mn	MnSO ₄	0.075	...
Fe ²⁺	FeSO ₄	0.240	+
Fe ³⁺	FeCl ₃	0.052	...
Zn	ZnSO ₄	0.060	...
Cu	CuSO ₄	0.840	++
Al	Al ₂ (SO ₄) ₃	0.071	...
Ni	Ni(NO ₃) ₂ ·6H ₂ O	0.078	...
Co	CoCl ₂ ·6H ₂ O	0.081	...
Pb	Pb(NO ₃) ₂	0.078	...
Sn	SnCl ₄ ·5H ₂ O	0.070	...
Ba	BaCl ₂ ·2H ₂ O	0.065	...
Se	metal	0.045	...
Se	acid solubilized	0.068	...
Mo	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	0.085	...
V	VC ₂ H ₃ O ₂	1.20	+++
Ag	AgNO ₃	1.45	+++
Hg	Hg(C ₂ H ₃ O ₂) ₂	0.430	+

^a Metallic salts tested at 100 ppm.

^b Metallic salts were reacted with 100 ppm KBrO₃ under the conditions of the screening procedure.

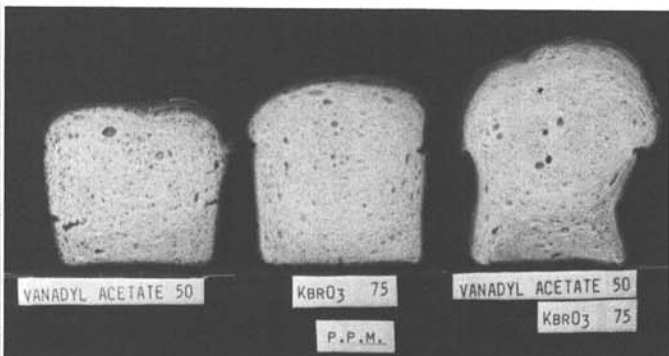


Fig. 2. Catalytic effect of the vanadium ion on KBrO₃ oxidation. Doughs were mixed at 63–65° F. Breads were made by the no-time baking method. **Left**, Bread made with 50 ppm vanadyl acetate; **center**, bread made with 75 ppm KBrO₃; **right**, bread made with 75 ppm KBrO₃ + 50 ppm vanadyl acetate.

sulfate concentration when combined with a constant level of KBrO₃ (Fig. 5). Additional baking experiments were conducted at ambient temperature, in order to separate the effect of the metal ions from KBrO₃, i.e., whether they operated as catalysts or as oxidants similar to bromate. Baking data clearly showed that copper did not function as a catalyst, but rather as an oxidant, operating in a manner similar to KBrO₃. Copper can operate alone as an oxidant in breadmaking (Table IV). In contrast, vanadium

TABLE III
Effect of Different Metallic Salts on KBrO₃ as Measured by Colorimetry and in Baking^a

Metallic Salt	Metallic Salt Concentration (ppm)	Absorbance (625 nm)	Specific Loaf Volume ^b (cm ³ /g)
None	0	0.035	5.1 ± 0.1
NaCl	100	0.055	5.2 ± 0.1
KCl	100	0.050	5.1 ± 0.1
CaSO ₄	100	0.060	5.2 ± 0.1
FeCl ₃	100	0.052	5.1 ± 0.1
ZnSO ₄	100	0.060	5.3 ± 0.1
VC ₂ H ₃ O ₂	10	1.20	... ± ...
VC ₂ H ₃ O ₂	50	...	6.8 ± 0.2
CuSO ₄	50	0.85	6.2 ± 0.2
FeSO ₄	100	0.24	5.7 ± 0.1

^a Doughs were mixed at 63–65° F and 4% less absorption water, then processed by the no-time baking method. KBrO₃ was used at 100 ppm in colorimetry and at 75 ppm in baking.

^b Mean of triplicate doughs tested on two different days ± standard deviation.

^c Made with 30% less dough mixing.

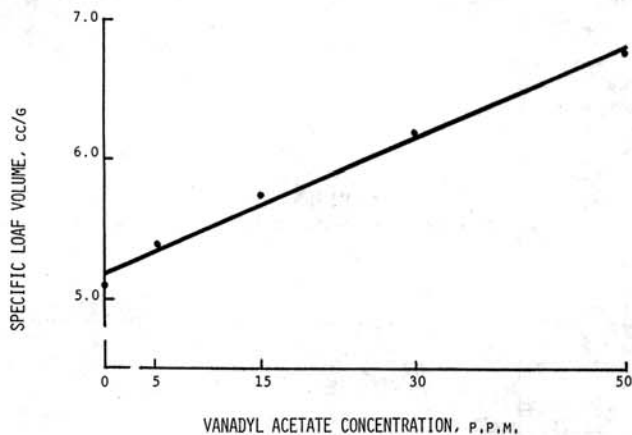


Fig. 3. Effect of vanadyl acetate concentration on specific loaf volume. Flour was treated with 75 ppm KBrO₃ + 0, 5, 15, 30, and 50 ppm vanadyl acetate. Doughs were mixed at 63–65° F. Breads were made by the no-time baking method.

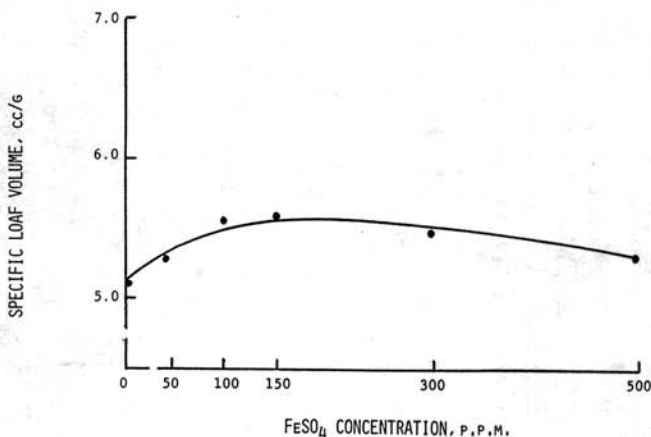


Fig. 4. Effect of ferrous sulfate concentration on specific loaf volume. Flour was treated with 75 ppm KBrO₃ + 0, 50, 100, 150, and 300 ppm ferrous sulfate (bakery grade). Doughs were mixed at 63–65° F. Breads were made by the no-time baking method.

(Table II; Fig. 2) and ferrous ions (Table V) exerted their effects as catalysts.

The catalytic effect of metal ions on KBrO_3 oxidation has definite implications in baking: 1) Bromate oxidation was accelerated. 2) Doughs containing catalytic metal ions required less bromate. 3) Variable ion concentration led to variable bromate requirements. 4) To prevent overoxidation, KBrO_3 should be in balance with the catalytic ion concentration.

Although vanadium is rarely found in wheat flour, it may occur in dough via water or ingredients. In contrast, copper and Fe^{2+} can reach a dough by way of flour, ingredients, water, or equipment. It is well documented in the literature that KBrO_3 decomposes to stable KBr in dough. Therefore, a typical bromated dough can accommodate both materials, rendering the catalytic action of metal ions obscure. The data in Table VI demonstrate unequivocally that metal ions, such as vanadium, catalyze the action of KBrO_3 and not KBr .

Data presented thus far have focused mainly on KBrO_3 . Baking experiments using vanadyl acetate were also conducted with other

TABLE IV
Comparison Between KBrO_3 and CuSO_4 Oxidation in Baking^a

KBrO_3 Concentration (ppm)	CuSO_4 Concentration (ppm)	Specific Loaf Volume ^b (cm^3/g)
0	0	4.8
5	0	5.0
0	5	5.1
20	0	5.5
0	20	6.0
40	0	6.0
0	40	6.5

^aDoughs were mixed at ambient temperature and optimum water absorption and processed by the no-time baking method.

^bTriplicate doughs tested on two different days (\bar{x}).

TABLE V
Effect of FeSO_4 on Bromate Oxidation in Baking^a

KBrO_3 Concentration (ppm)	FeSO_4 Concentration (ppm)	Specific Loaf Volume ^b (cm^3/g)
0	0	4.3 ± 0.1
0	100	4.4 ± 0.1
75	0	5.2 ± 0.1
75	100	5.8 ± 0.1

^aDoughs were mixed at 63–65°F and 4% less absorption water and processed by the no-time baking method.

^bMean of triplicate doughs tested on two different days \pm standard deviation.

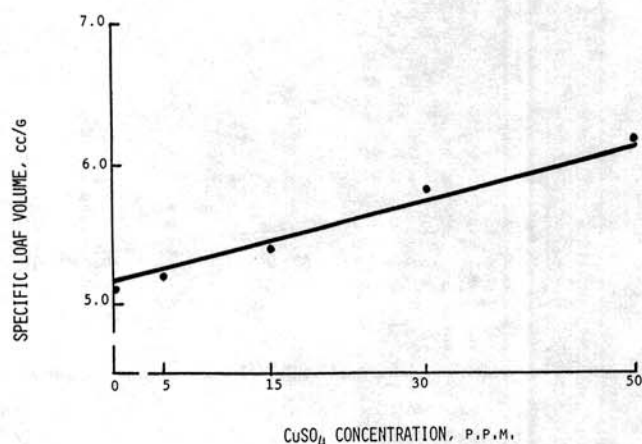


Fig. 5. Effect of cupric sulfate concentration on specific loaf volume. Flour was treated with 75 ppm KBrO_3 + 0, 5, 15, 30, and 50 ppm cupric sulfate. Doughs were mixed at 63–65°F. Breads were made by the no-time baking method.

oxidants, such as AA, potassium iodate KIO_3 , and ADA. These oxidants were evaluated colorimetrically and in baking (Table VII). Unlike KBrO_3 , the vanadium ion exhibited no catalytic

TABLE VI
Comparison of the Catalytic Effect of Vanadyl Acetate on KBrO_3 and KBr in Baking^a

KBrO_3 (ppm)	Concentration		Specific Loaf Volume (cm^3/g)
	KBr (ppm)	Vanadyl Acetate (ppm)	
75	0	0	5.2
0	75	0	4.4
75	0	50	6.6 ^b
0	75	50	4.6
75	75	50	6.8 ^b

^aDoughs were mixed at 63–65°F and 4% less absorption water, then processed by the no-time baking method.

^bMade with 30% less dough mixing.

TABLE VII
Catalytic Effect of Vanadyl Acetate on Different Oxidants as Measured by Colorimetry and in Baking^a

Oxidant/ Concentration (ppm)	Vanadyl Acetate ^b Concentration (ppm)	Absorbance (625 nm)	Specific Loaf Volume (cm^3/g)
None			
0	0	0.050	4.7
0	10	0.140	...
0	50	...	4.8
Ascorbic acid			
100	0	0.010	5.0
100	10	0.020	...
100	50	...	5.4
KIO_3			
100	0	0.045	5.3
100	10	0.150	...
50	50	...	5.4
KBrO_3			
100	0	0.054	5.2
100	10	1.28	...
75	50	...	6.4
ADA ^c			
100	0	0.330	5.7
100	10	1.80	...
45	50	...	6.6

^aDoughs were mixed at 63–65°F and 4% less absorption water, then processed by the no-time baking method.

^bDoughs containing vanadyl acetate received 30% less mixing.

^cAzodicarbonamide.

TABLE VIII
Comparison Between ADA^a and KBrO_3 Plus Increasing Concentrations of Vanadium on the Rate of Oxidation of DDA^b

Oxidant/ Concentration (ppm)	Vanadyl Acetate Concentration (ppm)	Absorbance ^c (625 nm)
None		
0	0	0.048
0	10	0.140
0	15	0.168
0	20	0.180
ADA		
20	0	0.330
20	10	0.780
KBrO_3		
20	0	0.054
20	10	0.420
20	15	0.620
20	20	0.770

^aAzodicarbonamide.

^b4, 4-Diaminodiphenylamine sulfate.

^cReaction time of 15 minutes at pH 5.00 under the conditions of the screening procedure. Mean of triplicate analyses.

action on either ascorbic acid or iodate. However, it did exert a positive effect on ADA. In fact, vanadium catalysis seemed to be slightly higher with ADA than KBrO_3 .

It is well known that ADA is a faster acting oxidant than KBrO_3 in breadmaking. This pattern was also obtained colorimetrically (Table VII). It is possible for KBrO_3 to act as rapidly as ADA (Table VIII) by increasing the concentration of the catalyst, e.g., ADA = 20 + vanadyl, Ac = 10 (ppm); versus KBrO_3 = 20 + vanadyl, Ac = 20 (ppm).

The catalytic effect of metal ions on bromate raises several important fundamental questions. The first is related to the mechanism by which vanadium and Fe^{2+} ions catalyze the bromate action. Oxidation-reduction reactions (electron transfer) may not be entirely the path of action, since KIO_3 was unaffected by these ions. Second, do copper and KBrO_3 (or other oxidants) act upon the same flour component(s)? If so, will chelating agents such as ethylenediaminetetraacetic acid arrest or reduce the bromate action in breadmaking?

In light of the fact that certain metal ions can catalyze the bromate reaction or replace it altogether (copper), the bromate mechanism needs to be reexamined. The bromate oxidation mechanism may not be a single event (oxidation of sulfhydryls to disulfides), but rather the collective end result of several different reactions involving different flour and dough components.

CONCLUSIONS

Various experiments were conducted with metal ions generally encountered during breadmaking. The test model chosen for this work was the no-time breadmaking method utilizing subambient (63–65°F) dough mixing conditions. In this type of environment, demands for oxidation are high, thus rendering the model very sensitive.

A rapid colorimetric method was developed that isolated metal ions with catalytic properties on KBrO_3 and ADA. Absorbances correlated well with baking results. Both colorimetry and baking identified vanadium and Fe^{2+} ions (or others not tested here) as having catalytic properties. Copper (alone) operated as an oxidant similar to KBrO_3 and did not function as a catalyst. The general

implications of these findings on baking are that presence of these ions will undoubtedly lead to variations in oxidation requirements (ADA, KBrO_3).

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