DISAPPEARANCE OF BROMATE DURING BAKING OF BREAD[1]

W. BUSHUK AND I. HLYNKA
With addendum by
C. C. LEE[2] AND R. TKACHUK

ABSTRACT

The amperometric titration method was applied to the study of the disappearance of bromate during baking of bread from bromated flour. For initial potassium bromate concentrations of 5 to 40 p.p.m., essentially no bromate was found in the bread crumb after a 10-minute baking period. For 80 p.p.m. a small amount of bromate was found after 15 minutes baking time; none was found after 20 and 25 minutes. Similar results were obtained for bread baked according to the formula of Lee *et al.* from flour containing 20 and 40 p.p.m. potassium bromate. Additional experiments by Lee and Tkachuk have reconciled their previous findings with those of this study.

Until recently, it has been the opinion of most cereal chemists that there was no residual bromate in bread baked from flour containing normal amounts of potassium bromate (4,5,8). In a recent study, Lee and Tkachuk (6) found that bread baked from flour treated with 5 to 30 p.p.m. of Br^{82}-labeled potassium bromate contained residual Br^{82} equivalent to 33 to 42% of the bromate added. They concluded that the residual radioactivity was due to bromate.

The present study was designed to reinvestigate the decomposition of bromate during the baking procedure and to check the presence of bromate in bread by the amperometric titration technique (2,3). The results that were obtained with initial concentrations from 5 to 80 p.p.m. of potassium bromate are reported in this paper.

Materials and Methods

The flour used in this study was a straight-grade flour, milled commercially from hard red spring wheat. It was described completely in a previous paper (2). The following baking formula was employed: 100 g. flour (14% moisture), 2.0 g. fresh yeast, 2.5 g. sucrose, 1.0 g. salt, 0.1 g. ammonium dihydrogen phosphate, 0.3 g. nondiastatic malt (250° Lintner), potassium bromate as required, and water to give 59.5% absorption. A separate dough was prepared for each bromate determination. The doughs were mixed, fermented, and proofed according to the basic baking test procedure (1). For comparison purposes, experiments with 0, 20, and 40 p.p.m. (flour basis) of potassium

[1] Manuscript received February 3, 1960. Paper No. 183 of the Grain Research Laboratory, Board of Grain Commissioners for Canada, Winnipeg 2, Canada.
[2] Department of Chemistry, University of Saskatchewan, Saskatoon, Sask., Canada.

bromate were made using the baking formula of Lee, Tkachuk, and Finlayson (7), which includes shortening and milk solids in addition to the materials listed above. The oven temperature was 220°C. in all baking experiments.

Ten-gram subsamples of dough (or bread crumb) were analyzed for bromate by the amperometric titration method (2,3) immediately after each of the following stages: mixing, first punch, second punch, panning and proofing, and at 5-minute intervals during baking. The quantity of dough (or crumb) was reduced to 10 g. to increase the clarity of the extracts, particularly in baked bread. Suspended materials in the extracts do not affect the end point, but tend to decrease the slope of the titration curve (μamp. vs. ml. of titrant) and accordingly decrease the accuracy of the titration. Three bromate analyses were made using the extraction procedure of Lee and Tkachuk (6) except that the treatment with bromine and extraction with carbon tetrachloride was omitted. All results were reported in parts of potassium bromate per million of flour containing 14% moisture.

Results and Discussion

Table I gives the amounts of bromate found in dough, given in p.p.m. of flour immediately after the steps in the baking procedure indicated. The amounts recovered after the loaves were put in the oven were not corrected for the drop in moisture during baking; the actual correction that could be applied is negligible, since the drop in moisture content of crumb during baking was only about 1%.

TABLE I

BROMATE RECOVERIES FROM DOUGH AND BREAD

BAKING STAGE[b]	BROMATE ADDED (p.p.m. flour)						
	5	10	20	20[a]	40	40[a]	80
	BROMATE RECOVERED (p.p.m. flour)						
Mix	4.61	9.73	19.46	17.92	36.10	34.30	73.73
First punch	4.10	8.70	17.15	16.90	33.28	32.00	68.10
Second punch	3.97	8.45	16.90	16.64	32.26	32.26	67.07
Pan	3.97	8.20	16.64	16.13	32.00	31.49	66.05
Proof	3.58	7.94	16.38	15.36	31.23	29.70	64.26
Oven (minutes)							
5	3.97	3.84	11.01	4.99	21.50	23.55	51.71
10	0.77	0.0	0.0	1.28	0.0	11.26	18.94
15	0.0	0.0	0.0	0.0	0.0	1.54	2.56
20	0.0	0.0	0.0	0.0	0.0	0.0	0.0
25	0.0	0.0	0.0	0.0	0.0	0.0	0.0

[a] Baking formula of Lee *et al.* (7).
[b] Analyses were made immediately after the various stages indicated.

The results of Table I show unequivocally that for initial potassium bromate concentrations up to 80 p.p.m., no bromate is demonstrable in bread after a 25-minute baking period. For 40 p.p.m. potassium bromate or lower, no bromate could be detected in the bread 10 minutes after the dough entered the oven. Essentially the same results were obtained for loaves prepared according to the formula of Lee and Tkachuk (6) containing initially 20 and 40 p.p.m. of potassium bromate. There is an indication that the length of time necessary for all the bromate to react increases with increasing initial bromate concentration; accordingly, it is quite possible that at some concentration higher than 80 p.p.m. part of the bromate would remain in the bread. For example, Freilich and Frey (4) found small amounts of the bromate in bread for the initial potassium bromate concentration of 100 p.p.m. and larger amounts in loaves containing initially 500 and 1,000 p.p.m. However, these concentrations exceed those encountered in baking practice.

The presence of bromate in the aqueous extract (prior to treatment with bromine and extraction with carbon tetrachloride), prepared according to the procedure of Lee and Tkachuk (6) from bread made from flour containing 30 p.p.m. potassium bromate, was checked by the amperometric titration method. No bromate could be detected. Potassium bromate, added to the bread crumb during extraction in the amount equivalent to 5 p.p.m., was completely recovered and there were no interfering substances extractable from bread that contained initially no bromate.

There seemed to be an obvious discrepancy between the results of this study and those of Lee and Tkachuk (6). A copy of this manuscript was made available to these authors at the time it was submitted for publication. In an attempt to reconcile the two sets of results Lee and Tkachuk undertook to check their results by further experiments with Br^{82}-labeled bromate. Their findings, which bring the previous results in line with those of this study, are included as an addendum.

Addendum by C. C. Lee and R. Tkachuk

A repetition of the work on the presence of bromate in bread baked with Br^{82}-labeled bromate but using a flour different from that employed previously (6) showed that there is no residual bromate in bread. The error in the earlier work (6) was likely due to an incomplete exchange of bromide with bromine under the conditions of those experiments. Although control tests showed that aqueous solutions of bromide exchanged readily with bromine, when bread was baked from dough containing Br^{82}-labeled potassium bromide, the bromide recovered in the aqueous bread extract could not be removed completely by one simple exchange with bromine.

For example, with the aqueous extract from bread originally containing 30 p.p.m. Br^{82}-labeled potassium bromide, one exchange treatment followed by extraction of the bromine with organic solvent removed only about 80% of the bromide. The residual bromide, however, could be removed by a second exchange treatment with bromine. Since no successive exchange treatments were carried out in the previous work (6), the bromide which was not removed by one exchange with bromine was mistakenly assumed to be bromate.

Acknowledgments

The authors wish to thank F. D. Kuzina who did the baking, and R. A. McLeod for the bromate analyses.

Literature Cited

1. American Association of Cereal Chemists. Cereal laboratory methods (6th ed.). The Association: St. Paul, Minnesota (1957).
2. Bushuk, W., and Hlynka, I. The bromate reaction in dough. I. Kinetic studies. Cereal Chem. **37:** 141–150 (1960).
3. Cunningham, D. K., and Anderson, J. A. Decomposition of bromate in fermenting and nonfermenting doughs. Cereal Chem. **33:** 290–299 (1956).
4. Freilich, J., and Frey, C. N. Dough oxidation and mixing studies. I. The action of potassium bromate in dough. Cereal Chem. **16:** 485–494 (1939).
5. Hlynka, I. [An answer given in the column "Problems in Baking."] Baker's Digest **31** (4): 84 (1957).
6. Lee, C. C., and Tkachuk, R. Studies with radioactive tracers. II. The presence of unchanged bromate in bread. Cereal Chem. **36:** 294–298 (1959).
7. Lee, C. C., Tkachuk, R., and Finlayson, A. J. The conversion of Br^{82}-labeled bromate to bromide in nonfermenting and fermenting doughs and in baked bread. Cereal Chem. **35:** 337–349 (1958).
8. Sullivan, Betty, Howe, Marjorie, Schmalz, F. D., and Astleford, G. R. The action of oxidizing and reducing agents on flour. Cereal Chem. **17:** 507–528 (1940).