METHYL BROMIDE FUMIGATION. I. EFFECT OF HIGH DOSAGES ON BREADMAKING QUALITY AND GERMINATION OF WHEAT

W. MINETT[1], R. A. ORTH[1], and L. J. COOK[2], Department of Agriculture, Victoria, 5 Parliament Place, Melbourne, Victoria, Australia

Cereal Chemistry 53(1): 41-50

ABSTRACT

Two samples of mixtures of the soft wheat varieties Pinnacle and Summit, and two of the hard wheat variety Emblem, were fumigated with methyl bromide at concentration-time products (CT) ranging from four to twenty times that used in normal practice. After duplicated milling on a Buhler experimental mill, the test baking loaf volumes and rheological properties of the resultant flours were determined. As expected, milling yield and the proportion of individual mill streams were not affected by methyl bromide treatment. Data obtained from rheological testing and determination of loaf volume for each wheat were subjected to analysis of variance. Fumigation caused a significant increase in maximum resistance to extension and a significant decrease in loaf volume. Fumigation reduced the germination vigor of all wheats studied. Although the total germination of the fumigated wheats was not significantly different from that of the control, except for CT values above 2200 mg.h/l, the rate of germination was affected by all fumigation doses studied. An inverse relation between germination vigor and fumigation dose was established.

Strains of the common species of grain insects in Australia have developed some degree of resistance to malathion, the commonly used grain protectant (1). Accordingly, alternative insecticides are required to guard against infestation of stored grain. One possible chemical for this purpose is the fumigant, methyl bromide.

The value of methyl bromide as a fumigant was first reported by Le Goupil (2) in 1932. Since then it has been widely used for this purpose. For example, in the

[1]Division of Agricultural Chemistry, Melbourne.
[2]Seed Testing Station, Burnley.

U.K. in 1964, 91% of all cereal grains and cereal products fumigated in ships, under sheets, or in chambers was treated with methyl bromide (3).

It has been established that approximately 80% of the methylation occurring during wheat fumigation involves wheat protein (4). Further studies (4,5) showed that the principal reactions between methyl bromide and flour protein were with the amino acids histidine, methionine, and cysteine. Fumigation with methyl bromide may be expected to cause changes in breadmaking quality parameters such as loaf volume and dough strength, since these properties depend on the chemical structure of, and interaction between, the flour proteins.

The effects of methyl bromide fumigation of wheat and wheat flour on breadmaking quality have received little attention. Shepard and Buzicky (6) reported no detectable injury to baking quality for flour fumigated with methyl bromide at commercially used concentration-time products (CT) (approximately 200 mg.h/l). Later studies by Hermitte and Shellenberger (7) showed that flour fumigated with excessive levels of methyl bromide (CT values of 9600 mg.h/l) underwent irreversible changes in breadmaking quality. Reduced dough development times, lowered mixing tolerances, and decreased loaf volumes were observed for fumigated samples.

More recent studies have involved the fumigation of wheat rather than flour. Fumigation of a hard red winter wheat at levels of about five times normal showed that baking quality was not affected by methyl bromide treatment (8). This conclusion was supported by a report on the effect of several fumigants, including methyl bromide, on breadmaking quality (9). Although changes in amylograph viscosity and farinograph mixing tolerance were observed for the methyl bromide treated samples, storage time had more influence on flour properties than did fumigation. No differences in loaf volume were detected.

An important consideration in the storage of seed wheat for commercial or experimental purposes is the effect of methyl bromide fumigation on total germination and germination vigor. It has been established that germination of a number of cereals is decreased by methyl bromide fumigation (3). Wheat was, in fact, the cereal with least tolerance to the fumigant (10).

The aim of the present study was to determine the effect of methyl bromide fumigation on the breadmaking quality and germination of hard and soft Victorian wheats. Dosages used were above normal but within the range possible in the practical situation.

MATERIALS AND METHODS

Wheat Samples

The wheats used were two samples of the hard wheat variety Emblem (abbreviated E1 and E2), and two of a mixture of the soft wheats Pinnacle and Summit (PS1 and PS2).

Methyl Bromide Fumigation

Table I lists the wheats, their protein contents, moistures, and the methyl bromide dosages used. The latter are expressed as concentration-time products since both the concentration of fumigant and the time of fumigation are factors in the overall sorption of the fumigant (11).

Wheat moisture has a major bearing on the extent of reaction between the wheat protein and the methyl bromide (12). In addition, changes in dough rheology due to fumigation of flour were influenced by flour moisture level (7). The moisture contents of the wheats used in this study are below world average, but typical of Australian storage conditions.

For each wheat, two dosages (A and B) and a nonfumigated control were prepared. The dosages used ranged from four to twenty times that recommended to achieve a high percentage kill of a wide range of grain insects (13).

Laboratory-scale fumigation was carried out as follows. The ampule of methyl bromide was cooled to between −10° and −18° C in a freezing mixture (3 parts ice to 1 part salt) before being opened. The appropriate aliquot of methyl bromide was withdrawn in a cold, graduated pipet and introduced into a small beaker placed on top of approximately 6 kg of wheat stored in an 8.6-l. capacity Duraglas jar at room temperature (20° C). The lids of the jars were sealed with plastic tape. The jars were then placed in a fume cupboard (20° C) for 48 hr before removing the lids and airing the wheat for a further 48 hr.

Dosages were calculated by multiplying the concentration of methyl bromide (milligram per liter of storage volume) by the fumigation time (hours).

Milling

After conditioning to 14.5% moisture for 24 hr for Pinnacle-Summit, and to 15.5% moisture for 48 hr for Emblem, the wheats were milled on a Buhler experimental mill, and flour yield calculated as a percentage of the total product. The first milling of each wheat was carried out within 2 weeks of fumigation, and the second milling 4 months after fumigation.

Rheological Testing

Farinograph and extensigraph tests were performed according to the standard AACC methods (14). Rheological testing and test baking were performed 1 month after the wheats were milled.

Baking Test

Because of worldwide variation in details of baking tests, the method used is outlined below.

Three hundred grams of flour, 1.5 g malt flour, 50 ml of a 12% w/v yeast solution, 3 ml of a solution containing 0.1% w/v potassium bromate and 0.5% w/v ammonium chloride, 30 ml of salt solution (20% w/v), and water to make up

TABLE I
Wheat Composition and Fumigation Dosages

Sample	Code	Protein % (as-is)	Moisture % (as-is)	Dose A mg.h/l	Dose B mg.h/l
Emblem	E 1	13.8	10.9	960	2200
Pinnacle-Summit	PS 1	8.7	11.1	960	2200
Emblem	E 2	12.5	11.4	1440	4320
Pinnacle-Summit	PS 2	11.7	11.5	960	3600

to baking absorption were mixed for 2.5 min in a farinograph bowl. After proofing at 26°C for 105 min, the dough was punched, then replaced in the proofing cabinet for 50 min. A second punch was performed and the dough placed in the cabinet for a further 25 min before panning. Fifty-five minutes later the dough was baked for 35 min in a rotary oven at 230°C. Loaf volumes were determined the following day by rapeseed displacement.

Germination Tests

Standard germination tests were conducted to see how the fumigation treatments affected seed viability. Four replicates, each of 100 seeds, were set out on moist seed-testing blotting paper, and maintained at 20°C. The seeds were regarded as germinated when the radical was 3–4 mm long. Germination was counted daily.

The Germination Index, a measure of germination vigor, is based on the Germination Resistance of Gordon (15), and combines a measure of the speed of germination and the total germination of seed. It is the weighted mean of the time taken to germinate in hours, converted to a range of 0 to 1, and then multiplied by total germination.

The formula for Gordon's Germination Resistance is:

$$GR = \frac{\frac{t_1 \times n_1}{2} + \frac{(t_1 + t_2)(n_2 - n_1)}{2} + \cdots \frac{(t_i + t_{i=1})(n_i - n_{i=1})}{2}}{n_i}$$

where n_1, n_2 and n_i are the cumulative percentage germination at times t_1, t_2, and t_i, where t is measured in hours.

If germination counts are made daily, this number can be converted to a range of 0 to 1 by the formula $(t_i - GR)/(t_i - 12)$ and multiplying this quantity by the total germination gives the Germination Index.

RESULTS AND DISCUSSION

Milling Quality

Because of the influence of milling extraction on flour quality (16), each wheat was milled twice. Each flour was then tested individually giving two sets of rheological and breadmaking quality data for each control and fumigated wheat.

The data were subjected to analysis of variance to determine whether significant differences in milling and breadmaking quality parameters existed between the control and fumigated wheats. Least significant differences, where calculated, are listed in the tables of results. Dose x variety interactions, when present, were not large, and only the main effects of fumigation are presented in Tables II and III.

Table II summarizes the milling results for the first milling of each wheat. Similar proportions of mill products were obtained for the second milling of each sample, but the figures are not included for the sake of brevity. Variation in per cent extraction existed between the first and second milling of each wheat, and the influence of this on flour properties is discussed later in this paper.

As expected, fumigation had no discernible effect on flour yield, nor on the relative proportions of the mill streams (bran, pollard, break, and reduction flour). This finding is in agreement with that of Shuey *et al.* (17) who concluded that the milling properties of a number of wheats were not affected by methyl bromide fumigation at dosages of 1200 to 2400 mg.h/l.

Consistent milling of the wheats of any one test group (*e.g.*, E1, E1A, E1B) was essential since significant differences in breadmaking quality and dough rheology have been demonstrated for laboratory-milled flours representing extraction rates differing by as little as 2% (16). The variation in milling yield for control and fumigated wheats of any one test group was less than 1%, and allowed measurement of the effect of fumigation alone on the breadmaking and rheological properties of the flours.

Dough Rheology

Table III summarizes the results of breadmaking quality tests. Analyses of variance of this data yielded the mean values and least significant differences listed below each variable. Mean values only are shown as we were interested in the general effect of fumigation on flour properties.

Farinograph water absorption and dough breakdown varied between treatments for each wheat, but the differences were relatively small and no trends were observed with fumigation. Dough development time either decreased with fumigation or no change was detected. Fumigation did not cause an increase in this parameter for any wheat studied.

TABLE II
Mean Values of Milling Parameters

Treatment	Wheat g	Pollard g	Bran g	Flour g	Total Product g	% Extraction
Control	2682	323	441	1837	2601	71
Dose A	2686	317	446	1856	2619	71
Dose B	2687	320	432	1840	2592	71

TABLE III
Mean Values of Dough Rheology and Breadmaking Quality Parameters

Treatment	Water Absorption %	Dough Breakdown BU	Dough Development Time min	Extensibility cm	R_{max} BU	Loaf Volume
Control	65.6	65	4.7	20.3	276	1872
Dose A	65.6	66	4.6	19.8	293	1791**
Dose B	65.5	61	4.2	20.1	310*	1791**
Least Significant Differences						
5%	1.3	11	0.8	1.2	27	31
1%	1.8	15	1.1	1.7	38	44

The greatest differences between the control and fumigated wheats were observed in extensigraph tests of the flours. Both extensibility and maximum resistance to extension (R_{max}) varied significantly between samples. The former variations did not fit any pattern as is apparent from the similar mean values for each treatment for this variable (Table III).

A consistent increase in maximum resistance to extension was noted for the flours from fumigated wheats. This increase averaged approximately 20 Brabender Units (BU) for Emblem in the first fumigation, and 35 BU in the second fumigation. Corresponding increases for the Pinnacle-Summit mixtures were 35 and 50 BU. This finding indicates that the weaker Pinnacle-Summit dough responded slightly more to fumigation than did the relatively strong Emblem dough.

Although the resistances at 5 cm were only slightly higher for fumigated samples compared with the control, the maximum resistances were markedly higher. This effect was a general pattern for the flours of all fumigated wheats when compared to their respective controls. Maximum resistance was the most sensitive measurement of those used to detect changes in dough properties due to fumigation. The mean maximum resistance for dose B was significantly higher ($P \leqslant 0.05$) than that for the control.

Hermitte and Shellenberger (7) observed that methyl bromide dosages 12 to 25 times greater than those normally used reduced dough development times and lowered mixing tolerances. Shuey *et al.* (17) concluded that fumigation at levels comparable to those used in this study produced no deleterious effects on the milling or baking properties of the samples tested. Calderon *et al.* (8) and Matthews *et al.* (9) came to similar conclusions. The data of Matthews *et al.* are difficult to interpret, however, since no mention is made of the duration of fumigation in their report, making calculation of a CT value impossible.

Loaf Volume

The mean loaf volumes of the fumigated wheats were significantly lower than that for the control ($P \leqslant 0.01$). No significant difference was noted between dosage levels for this parameter (see Table III).

No objectionable odor was apparent at any stage of baking, and no other major variation in quality was noted. This result is in agreement with that of Hermitte and Shellenberger (7), who observed odors from bread baked from flour fumigated at a dosage of 9600 mg.h/l but not from flour fumigated at levels comparable to those used in this study.

When flour was treated with excessive levels of methyl bromide (7) (double the maximum dosage used in the present study), loaf volume decreases of greater than 15% were observed. The fact that flour rather than wheat was fumigated also tended to amplify the effects of methyl bromide on the dough properties because of the greater surface area of the former.

The work of Calderon *et al.* (8) is in disagreement with this report, however. These authors concluded that methyl bromide fumigation at a CT of 3600 mg.h/l had no effect on baking quality.

Germination

The cumulative daily germination of each fumigation treatment is presented in Fig. 1a for Pinnacle-Summit and Fig. 1b for Emblem.

Methyl bromide fumigation at the doses used in this experiment significantly slowed the rate of germination of the wheat.and, in general, the higher the dose, the slower the germination. The total germination of all treatments, except 2B, was not significantly different from that of the control. Treatment 2B was the highest fumigation dose for both varieties (4320 mg.h/l for Emblem and 2600 mg.h/l for Pinnacle-Summit) and, at these levels, more than 70% of the embryos were inactivated.

Figure 2 shows the Germination Index plotted against dose. A decrease in seed vigor with an increase in fumigation dose is apparent.

When these results are compared with those in Figs. 1a and 1b, an interesting fact emerges. Although the total germinations of samples 1A, 1B, and 2A for both wheats were not significantly different from their controls, there was a marked decrease in germination vigor for all treated wheats. At the higher dose

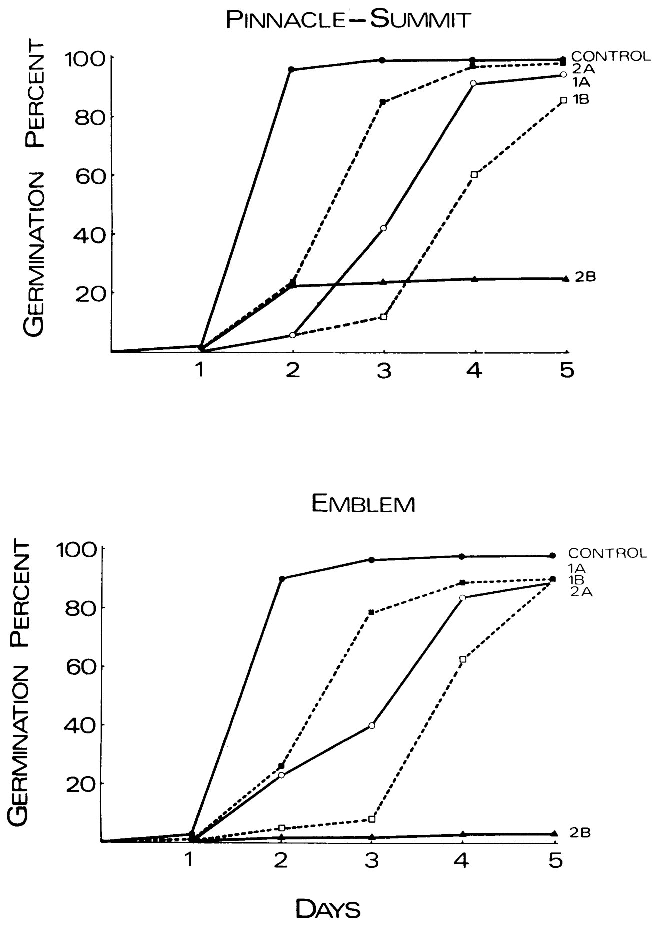

Fig. 1. Cumulative daily germination for (a) Pinnacle-Summit and (b) Emblem wheats fumigated at various doses (see Table I).

levels used on sample 2B of each wheat, very low germination per cent and germination index values were obtained. Apparently up to a fumigation dose of approximately 2000 mg.h/l the seed can recover from the effects of methyl bromide and germination per cent is not greatly reduced. Above this level, the effect of methyl bromide on germination is irreversible.

These results are in agreement with those of Lubatti and Blackith (18) who found that the germination of wheat at 11% moisture content was seriously affected by CT products of 1200 and 600 mg.h/l. In a subsequent study, Blackith and Lubatti (19) determined the germination per cent for wheats 3 and 6 years after fumigation. The wheats retained their germination capacity over the storage period. Whitney *et al.* (10) investigated the comparative germination tolerance of a number of cereals to methyl bromide. Wheat was the least tolerant, followed by maize, sorghum, barley, and oats.

CONCLUSIONS

Methyl bromide fumigation of four wheat samples showed that fumigation at levels between four and twenty times that used commercially was detrimental to breadmaking quality. The properties most sensitive to fumigation were extensigraph maximum resistance and breadmaking loaf volume. An increase in maximum resistance to extension of about 10% for Emblem and 20% for doughs of the Pinnacle-Summit fumigated wheats was observed.

Dough development times either decreased for the fumigated samples compared to the controls or remained the same. In no case did fumigation result in an increased dough development time. Changes in this parameter were difficult to measure for the PS1 series because of the low values obtained for these flours. Flours of the other series showed consistent decreases of over 0.5 min, and up to 1.5 min, except for the E2-1st milling series where dough development times were the same despite fumigation.

The increase in maximum resistance and indication of a slight decrease in

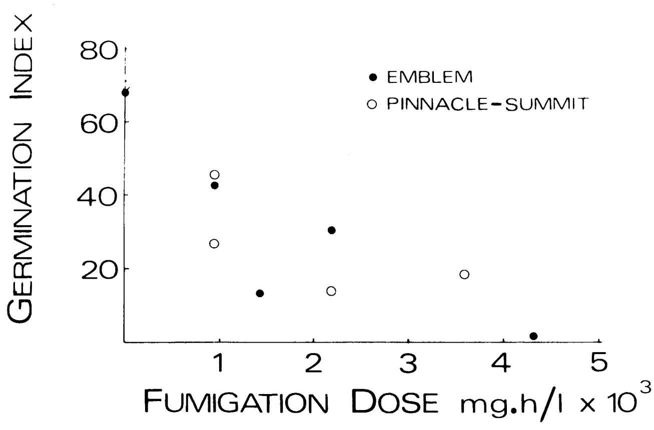

Fig. 2. Effect of fumigation dose on germination index of Emblem and Pinnacle-Summit wheats.

dough development time for the doughs of fumigated wheats suggest that chemical blocking of SH groups, by methylation, has affected dough properties. Although only a small proportion of the SH groups of the flour protein are methylated during fumigation (20), there is evidence from studies with N-ethylmaleimide (NEMI) to suggest that this may be sufficient to cause the observed changes.

Bushuk and Hlynka (21) and Sullivan *et al.* (22) reported that NEMI added to doughs in low concentrations (0.4 μeq per g of flour) caused increased extensigraph resistance.

Loaf volume depressions of greater than 5% of the control loaf volume were obtained for the fumigated wheats. These decreases were statistically significant within the 95% confidence limit. Decreases of this magnitude are large enough to cause concern, but it must be kept in mind that the fumigation doses used in this study were excessive.

It is difficult and somewhat dangerous to extrapolate laboratory results to field conditions, but it is likely that dose rates of above 1000 mg.h/l could reduce field establishment of wheat, particularly if the seed were subjected to very unfavorable growing conditions (very cold and/or very wet) after sowing. However, under normal weather conditions, dose rates of up to 1000 mg.h/l should not unduly affect field establishment. From this point of view then, methyl bromide has a relatively wide safety margin as a fumigant.

Although the dosage levels used were greater than normal, the results above indicate that methyl bromide fumigation of wheat should be carefully controlled. The minimum dosage used (four times normal) caused small, yet significant decreases in dough rheological properties, breadmaking quality, and germination vigor.

Acknowledgment

This work was financed by the Wheat Industry Research Council, Australia.

Literature Cited

1. CHAMP, B. R., and CAMPBELL-BROWN, M. J. Insecticide resistance in Australian *Tribolium castaneum* (Herbst) (Coleoptera, Tenebrionidae). II Malathion resistance in Eastern Australia. J. Stored Prod. Res. 6: 111 (1970).
2. LE GOUPIL, P. Les proprietes insecticides du bromure de methyle. Rev. Pathol. Veg. 19: 167 (1932).
3. THOMPSON, R. H. A review of the properties and usage of methyl bromide as a fumigant. J. Stored Prod. Res. 1: 353 (1966).
4. WINTERINGHAM, F. P. W., HARRISON, A., BRIDGES, R. G., and BRIDGES, P. R. Nature of methyl bromide residues in fumigated wheat. J. Sci. Food Agr. 6: 251 (1955).
5. BRIDGES, R. G. N-methylation as a result of fumigating wheat with methyl bromide. J. Sci. Food Agr. 6: 261 (1955).
6. SHEPARD, H. H., and BUZICKY, A. W. Further studies on methyl bromide as an insect fumigant. J. Econ. Entomol. 42: 854 (1939).
7. HERMITTE, J. J., and SHELLENBERGER, J. A. Effect of excessive methyl bromide fumigation on flour. Cereal Chem. 24: 449 (1947).
8. CALDERON, M., NAVARRO, S., and LINDNER, Z. Effect of common fumigants on the baking qualities of wheat. Cereal Chem. 47: 422 (1970).
9. MATTHEWS, R. H., FIFIELD, C. C., HARTSING, T. F., STOREY, C. L., and DENNIS, N. M. Effects of fumigation on wheat storage. II. Physical measurements of flour. Cereal Chem. 47: 579 (1970).

10. WHITNEY, W. K., JANTZ, O. K., and BULGER, C. S. Effects of methyl bromide fumigation on the viability of barley, corn, grain sorghum, oats and wheat seeds. J. Econ. Entomol. 51: 847 (1958).
11. MONRO, H. A. U. Manual of fumigation for insect control. FAO: Rome (1969).
12. VINCENT, L. E., and LINDGREN, D. L. Comparison of the sorption of hydrogen phosphide, methyl bromide, ethylene dibromide, and hydrocyanic acid by wheat and corn of different moisture contents and load factors. J. Econ. Entomol. 64: 122 (1971).
13. PEST INFESTATION CONTROL LABORATORY. Methyl bromide dosage schedules. Trop. Stored. Prod. Inf., Tolworth, England, p. 27 (1972).
14. AMERICAN ASSOCIATION OF CEREAL CHEMISTS. Approved methods of the AACC. The Association: St. Paul, Minn. (1962).
15. GORDON, A. G. The germination resistance test—a new test for measuring germination quality of cereals. Can. J. Plant Sci. 51: 181 (1971).
16. ORTH, R. A., and MANDER, K. C. Effect of milling yield on flour composition and breadmaking quality. Cereal Chem. 52: 305 (1975).
17. SHUEY, W. C., YOUNGS, V. L., and GETZENDANER, M. E. Bromide residues in flour streams milled from fumigated wheats. Cereal Chem. 48: 34 (1971).
18. LUBATTI, O. F., and BLACKITH, R. E. Germination and growth of cereals fumigated with methyl bromide. J. Sci. Food Agr. 8: 691 (1957).
19. BLACKITH, R. E., and LUBATTI, O. F. Prolonged storage of cereals fumigated with methyl bromide. J. Sci. Food Agr. 16: 455 (1965).
20. WINTERINGHAM, F. P. W. The fate of labelled insecticide residues on food products. IV. The possible toxicological and nutritional significance of fumigating wheat with methyl bromide. J. Sci. Food Agr. 6: 269 (1955).
21. BUSHUK, W., and HLYNKA, I. The effect of iodate and N-ethylmaleimide on extensigraph properties of dough. Cereal Chem. 39: 189 (1962).
22. SULLIVAN, B., DAHLE, L. K., and SCHIPKE, J. H. The oxidation of wheat flour. IV. Labile and nonlabile sulfhydryl groups. Cereal Chem. 40: 515 (1963).

[Received November 11, 1974. Accepted April 14, 1975]