Bromide Residues in Flour Streams Milled from Fumigated Wheats[1]

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ABSTRACT

Methyl bromide residues were determined on four milled products obtained from experimentally milled wheats treated with 1.5 and 3.0 lb. methyl bromide per 1,000 cu. ft. and at approximately 30 and 85% r.h. The fractions derived from the exterior portion of the kernel and those with higher lipid content contained higher amounts of residue. Higher amounts of applied methyl bromide resulted in higher amounts of residue. The milling and baking properties did not appear to be affected by the treatments applied. In general, neither variety nor class of wheat responded differently. The amount of residue also did not appear to be related to the degree of unsaturation of the lipid content.

The use of fumigants as a means of controlling insect pests is widely used by the food industry. Because of the increased use of these fumigants, more emphasis is now being placed on their residues in the finished product.

Getzendaner et al. (1) determined the bromide residues for a wide variety of food commodities fumigated with methyl bromide. Seefeld and Beitz (2) studied the dynamics of methyl bromide residue in small grains and other field crops. Hermitte and Shellenberger (3) reported the effect on flour of fumigating with excessive amounts of methyl bromide. Gibich and Pedersen (4) compared the bromide levels in mill fractions of unfumigated and fumigated HRW and HRS wheat mixes. The data clearly show that bromide residues exist in different amounts, with the effect of the residue dependent upon the method of application and the product to which it is applied.

The purpose of this study was to determine: 1) if wheat classes and varieties had different responses to fumigation, 2) the effect of relative humidity and amount of methyl bromide applied on the amount of residue, and 3) the distribution of the residues in the mill streams of broad classifications.

MATERIALS AND METHODS

Four spring wheats (Chris, Justin, Rescue, and Thatcher), one hard winter wheat (Scout), and one soft winter wheat (Seneca) were used in this study. The clean, dry wheat samples were divided into five 20-lb. lots.

The samples were treated with methyl bromide at two different levels (1.5 lb.

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per 1,000 cu. ft. and 3 lb. per 1,000 cu. ft.), and at two relative humidities (approximately 30 and 85%). The method of measuring the methyl bromide was essentially that of Childs and Press (5). The fumigation chamber was an autoclave with a volume of 59.5 cu. ft. A series of wheat samples was placed in the autoclave which was then evacuated with a vacuum pump to a vacuum of 11 in. of mercury. The ambient air in the room was adjusted to the desired temperature and relative humidity. The measured amount of methyl bromide then was added to the evacuated chamber through a valve. Immediately after the introduction of the methyl bromide, the chamber was brought to atmospheric pressure with the ambient air of the room. The valve was closed again, and the grain remained in the chamber for 48 hr.

The treated samples and the untreated control samples were milled on a Buhler experimental mill (6). The bran was rebolted over an 18W sieve; the overs were classified as bran and the thrus as shorts. The regular shorts, low grade, and 3rd break flour streams were blended and classified as low grade. The 1st, 2nd, and 3rd reduction flours were combined with the 1st and 2nd break flours for the patent flour.

The analytical results were obtained by procedures found in AACC Approved Methods (7).

The X-ray fluorescence method described by Getzendaner (1,8) was used to determine bromide residues.

For fatty acid analysis, the lipids were extracted by shaking the flour and different mill streams in chloroform. The fatty acids present, both free and esterified, were methylated with boron trifluoride by the method of Medcalfe and Schmitz (9). Analysis of the methyl esters was performed on a Barber-Coleman gas chromatograph equipped with flame ionization, and an 8-ft. glass column packed with 13% diethylene glycol succinate on 100/120-mesh Gas-Chrom Q diatomaceous earth. The carrier gas was nitrogen and the column was maintained at 198°C. Peaks were identified by comparing relative retention times of the unknowns with standards under identical operating conditions.

RESULTS AND DISCUSSION

Representative milling results are given in Table I. Cumulative ash curves of a given variety were very similar for the various levels of treatment. There were differences in the curves for the different varieties and classes of wheats. However, variations observed in the curves for a given variety with the various fumigation treatments were within experimental error. The milling data indicated that fumigating wheat with methyl bromide does not affect the milling properties appreciably.

In Table II are the data for the residue in p.p.m. of bromide found in the various mill fractions. These data show that a higher amount of methyl bromide increased the bromide residue content in the various fractions. A higher relative humidity at the time of application of the methyl bromide appeared to increase the amount of bromide residue content also, but not to the extent of larger amounts of methyl bromide. If the wheat had been exposed to the ambient conditions for long periods of time prior to fumigation, the results could have been different owing to different moisture contents in the wheat. This condition was not investigated. The shorts contained the greatest amount of residue; flour the least. Bran contained more

TABLE I. MILLING DATA OF FUMIGATED WHEAT SAMPLES

Variety	Treatment[a]	Pat. Ext. %	Pat. Ash[b] %	Total Yield %	Straight-Grade Flour Ash[b] %
Chris	A	61.5	0.365	71.8	0.485
	B	60.3	0.370	72.3	0.490
	C	60.7	0.360	72.0	0.485
	D	60.1	0.355	72.0	0.480
	E	61.0	0.365	72.2	0.495
Justin	A	62.1	0.355	71.2	0.500
	B	61.9	0.350	71.4	0.495
	C	62.4	0.355	71.1	0.495
	D	61.8	0.345	71.4	0.490
	E	62.4	0.360	71.3	0.515
Scout	A	63.4	0.330	72.6	0.420
	B	65.4	0.320	72.6	0.415
	C	66.5	0.335	72.8	0.425
	D	66.3	0.330	73.0	0.425
	E	66.2	0.340	72.7	0.435
Seneca	A	59.5	0.330	66.9	0.440
	B	61.0	0.325	68.0	0.455
	C	61.3	0.360	68.8	0.480
	D	61.3	0.320	69.0	0.455
	E	62.7	0.365	68.5	0.495

[a]A, control; B, 1.5 lb. methyl bromide per 1,000 cu. ft., 27% r.h.; C, 1.5 lb. methyl bromide per 1,000 cu. ft., 81% r.h.; D, 3.0 lb. methyl bromide per 1,000 cu. ft., 34% r.h.; E, 3.0 lb. methyl bromide per 1,000 cu. ft., 86% r.h.

[b]14% Moisture basis.

residue than the low grade stream and both were intermediate to the flour and shorts streams. These data concur with that of Gibich and Pedersen (4), who used regular mill mixes instead of pure varieties.

Since bromide residue appeared in the mill streams having high lipid content, analyses were performed to determine the effect on unsaturation of fatty acids. In Table III are the results of fatty acid analysis of Justin flour, bran, and shorts at the different treatment levels. No significant differences were noted when the methyl bromide was added at two different levels and at two different relative humidities. The same general pattern was true for the other varieties tested, as shown in part in Tables IV, V, and VI. Differences in fatty acid values did exist when the lipids of the bran, shorts, and flour were compared; linoleic acid, in particular, was less abundant in the bran and shorts than it was in the flour in all varieties. The opposite was true for oleic acid. On the basis of these results, the unsaturation of the lipids in flour, bran, and germ is not affected by fumigation with methyl bromide.

To further check the effect of fumigation, these same samples were baked. The baking results showed no adverse effect on the baking properties of the flour owing to the treatment of the wheat with methyl bromide prior to milling. Although some variations existed, no definite pattern could be established.

It was concluded from this study that, in general, neither varieties nor classes of wheat respond appreciably different to treatments of methyl bromide. These

TABLE II. RESIDUE IN p.p.m. OF BROMIDE IN THE VARIOUS MILL FRACTIONS

Variety	Treatment[a]	Bran	Shorts	Low Grade	Flour
Chris	A	<5	<5	<5	<5
	B	28	63	18	10
	C	32	66	19	10
	D	60	101	28	11
	E	55	111	35	11
Justin	A	<5	<5	<5	<5
	B	31	54	16	6
	C	37	75	19	7
	D	57	95	29	12
	E	62	111	37	10
Scout	A	10	7	7	8
	B	39	47	18	15
	C	36	55	21	15
	D	54	79	33	20
	E	61	89	34	20
Seneca	A	<5	<5	<5	<5
	B	28	52	25	7
	C	24	62	28	8
	D	38	93	48	14
	E	48	90	57	19

[a]A, Control; B, 1.5 lb. methyl bromide per 1,000 cu. ft., 27% r.h.; C, 1.5 lb. methyl bromide per 1,000 cu. ft., 81% r.h.; D, 3.0 lb. methyl bromide per 1,000 cu. ft., 34% r.h.; E, 3.0 lb. methyl bromide per 1,000 cu. ft., 86% r.h.

TABLE III. FATTY ACID ANALYSIS OF STREAMS MILLED FROM FUMIGATED JUSTIN WHEAT

Sample	Treatment[a]	Palmitic %	Stearic %	Oleic %	Linoleic %	Linolenic %
Flour	A	19.8	0.9	12.8	64.7	2.4
	B	20.3	0.6	12.1	64.9	2.1
	C	22.0	0.8	13.2	62.0	1.9
	D	20.9	0.5	13.1	64.0	1.4
	E	20.4	0.7	12.2	64.1	2.6
Bran	A	20.9	1.0	20.2	54.6	3.3
	B	19.7	0.9	19.3	55.5	4.6
	C	18.3	1.0	19.7	55.9	5.1
	D	21.5	0.6	19.8	54.4	3.6
	E	19.6	0.8	19.7	57.2	2.7
Shorts	A	20.1	0.8	18.0	56.8	4.3
	B	22.7	0.4	17.3	55.4	4.1
	C	20.5	0.6	18.3	55.6	5.0
	D	20.7	0.5	17.6	56.4	4.8
	E	20.7	0.5	17.0	56.6	5.1

[a]A, Control; B, 1.5 lb. methyl bromide per 1,000 cu. ft., 27% r.h.; C, 1.5 lb. methyl bromide per 1,000 cu. ft., 81% r.h.; D, 3.0 lb. methyl bromide per 1,000 cu. ft., 34% r.h.; E, 3.0 lb. methyl bromide per 1,000 cu. ft., 86% r.h.

TABLE IV. FATTY ACID ANALYSIS OF BRAN MILLED FROM FUMIGATED WHEAT

Acid	Treatment[a]	Chris %	Justin %	Scout %	Seneca %
Palmitic	A	18.1	20.9	19.4	19.0
	D	17.9	21.5	18.9	19.9
Stearic	A	1.1	1.0	0.5	0.9
	D	1.3	0.6	0.6	1.2
Oleic	A	21.2	20.2	18.1	19.5
	D	20.7	19.8	17.2	19.4
Linoleic	A	57.3	54.6	58.7	57.8
	D	56.8	54.4	59.0	56.5
Linolenic	A	2.4	3.3	3.4	3.0
	D	3.4	3.6	4.2	3.1

[a]A, Control; D, 3.0 lb. methyl bromide per 1,000 cu. ft., 34% r.h.

TABLE V. FATTY ACID ANALYSIS OF SHORTS MILLED FROM FUMIGATED WHEAT

Acid	Treatment[a]	Chris %	Justin %	Scout %	Seneca %
Palmitic	A	18.5	20.1	19.6	21.3
	D	20.1	20.7	19.5	21.2
Stearic	A	0.7	0.8	0.6	0.8
	D	0.8	0.5	0.6	1.0
Oleic	A	17.8	18.0	17.4	17.9
	D	18.8	17.6	17.2	17.6
Linoleic	A	58.3	56.8	59.0	56.4
	D	56.3	56.4	58.8	55.7
Linolenic	A	4.7	4.3	3.5	3.8
	D	4.0	4.8	4.0	4.7

[a]A, Control; D, 3.0 lb. methyl bromide per 1,000 cu. ft., 34% r.h.

TABLE VI. FATTY ACID ANALYSIS OF FLOUR MILLED FROM FUMIGATED WHEAT

Acid	Treatment[a]	Chris %	Justin %	Scout %	Seneca %
Palmitic	A	17.9	19.8	20.2	24.1
	D	19.2	20.9	21.4	23.7
Stearic	A	1.2	0.9	1.1	1.1
	D	0.9	0.5	0.6	1.3
Oleic	A	14.7	12.8	11.8	12.1
	D	12.8	13.1	11.8	12.4
Linoleic	A	63.8	64.7	63.3	60.7
	D	65.6	64.0	62.7	60.4
Linolenic	A	2.4	2.4	3.7	2.0
	D	1.5	1.4	3.6	2.2

[a]A, Control; D, 3.0 lb. methyl bromide per 1,000 cu. ft., 34% r.h.

studies indicated that there was a definite difference in the amount of residue in the various stream fractions. Those streams derived from the exterior portions of the kernel, particularly the bran and germ, contained more residue owing to a greater exposure to the fumigant. Those streams with higher lipid content contained higher amounts of residue; however, this did not appear to affect the unsaturation of the lipids. The higher the amount of methyl bromide applied to the wheat, the higher the amount of residue in the mill streams. At these levels of application there did not appear to be any deleterious effect on the milling or baking properties of the samples tested.

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