Penetration, Sorption, and Desorption of Fumigant in the Treatment of Food Materials with a Methyl Bromide–Acrylonitrile Mixture

When peanuts, corn, wheat, and wheat flour were treated with a 70:30 methyl bromide–acrylonitrile fumigant mixture, the methyl bromide penetrated through the materials at a faster rate than acrylonitrile at both 25 and 0 °C. Measurement of sorption of methyl bromide from the mixture by commodity treated at 25 °C showed that flour absorbed the highest quantity and corn the least. At 0 °C sorption was similar for all three seed commodities, with one-half the total amount applied being taken up, but with flour all of the methyl bromide was sorbed. Acrylonitrile was sorbed completely in nearly all cases. During the aeration of the materials (excluding flour) methyl bromide was desorbed completely in a few hours at both temperatures. However, acrylonitrile took many days to desorb depending on the type of commodity and the aeration conditions. Desorption was most rapid from peanuts, taking 7 days, and slowest from wheat, taking 21 days. The rate of desorption was greatly increased in samples of wheat that had been pretreated by a nitrogen aeration or by a heat treatment at 110 °C before fumigation.

The toxicity of fumigants to insects is reduced at low temperatures so that larger quantities are needed to obtain control as conditions become colder. Tests of fumigants have shown that the toxicity of certain materials can be improved when they are mixed. One of the fumigants which is extensively used to control insects in stored products, methyl bromide, is not very effective at freezing temperatures (Bond, 1975) but addition of acrylonitrile greatly increases toxicity, especially at low temperatures (Bond and Buckland, 1977). Concentrations of acrylonitrile used were much below the flammability range and the methyl bromide, being a fire suppressant, further increased the safety of the mixture. Tests made on insects in a 525-L chamber, where no commodity was present to interfere with penetration and loss of fumigant through sorption and residue formation, showed that insects could be effectively controlled over a range of temperatures down to −12.2 °C.

Since diffusion and penetration of gases are slowed down as temperature drops more fumigant is sorbed and retained in the commodity for longer periods of time at low temperature. Furthermore, components of a mixture may separate to move and penetrate at different rates, particularly at low temperatures, so that the quantity of each component may vary in different parts of the system. Studies were made on a 70:30 methyl bromide–acrylonitrile mixture to determine the penetration, sorption, and desorption of components of the mixture during fumigation and to establish the quantities of residue by the different commodities.

MATERIALS AND METHODS

Soft winter wheat, all purpose flour, feed corn, and raw in-shell peanuts were fumigated for 8 h at 25 and 0 °C with a range of concentrations of 70:30 methyl bromide–acrylonitrile in glass desiccators about 6 L in volume. The commodity was placed on filter paper on the perforated plate in the desiccator leaving free space above and below the material. Sampling points for withdrawing gas samples were made by drilling 5-mm diameter holes on the top and near the base of the desiccators and inserting silicone rubber stoppers. A watch glass 6 mm thick and 10 cm in diameter was preheated to 60 °C and placed on top of the commodity to receive the liquid fumigant. The acrylonitrile was injected as a liquid through the top sampling point to this glass and methyl bromide was then injected by a gas syringe into the space at the same sampling point. Vaporization of the liquid was completed in less than 10 min even when the dosage was high and temperature of the desiccator was 0 °C.

During the treatment, samples of the fumigants in the free space were analyzed by gas chromatography to determine penetration and sorption of the gases in the commodity. The instrument used was a Bendix 2300 gas chromatograph with a 2.5-m stainless steel column, 3 mm diameter packed with 30% didecyl phthalate liquid phase on Chromosorb W, 30/60 mesh, and a flame ionization detector. Using nitrogen as the carrier gas at a flow rate of 30 cm^3/min and a column temperature of 80 °C the retention time for methyl bromide was 1.2 min and that for acrylonitrile was 2.9 min. Full-scale deflection on a 25-cm 1-mV recorder was given by 5 ng of methyl bromide and 270 ng of acrylonitrile. At the end of the fumigation all the commodities except the flour were aerated and tested for desorption of fumigant.

Residual acrylonitrile was determined by placing 30 g of wheat, corn, or peanut kernels in 150-mL Erlenmeyer flasks with 35 mL of solvent or 10 g of peanut shell in 100 mL of solvent. The solvent was 5:1 v/v acetone–water as used by Heuser and Scudamore (1969). After standing overnight an aliquot was injected into the gas chromatograph. For this analysis the column (stainless steel, 3 mm diameter × 2.5 m long) was packed with Carbowax 20M, 25%, on Anakron AB, 80/100 mesh, solid support and the detector was alkali flame ionization. At a temperature of 70 °C with nitrogen carrier at a flow rate of 30 cm^3/min the retention time was 5.3 min for acrylonitrile. Under optimum conditions 40 ng of acrylonitrile gave full-scale deflection on a 25-cm 1-mV recorder. All peak areas were calculated by a Varian Aerograph 475 digital integrator. To determine the reproducibility of the analysis wheat was aerated for 0.25 h and four replicate samples were taken for each analysis.

The effect of acrylonitrile penetration alone or in a mixture with other gases was tested using methyl bromide or carbon dioxide.

RESULTS AND DISCUSSION

The length of time required for the methyl bromide–acrylonitrile mixture to penetrate a layer of wheat at 25 °C to the same concentration on both sides of the commodity is shown in Table I. Samples drawn from above and below the wheat at various times and analyzed in the gas chromatograph showed that sorption of fumigant, as indicated by a decrease in concentration in the free space, was a function of the amount of wheat present with all other conditions constant. In the treatment with 10 mg/L the total quantity of methyl bromide in the free space dropped from 42 to 39.4 mg in the desiccator containing 500 g of wheat and to 19 mg when 2500 g of wheat was

Table I. Penetration and Sorption of Methyl Bromide and Acrylonitrile in Wheat Treated in 6-L Desiccators for 8 h at 25 °C with 70% Methyl Bromide–30% Acrylonitrile Mixture

Dosage, mg/L	Quantity of wheat		Penetration time, [a] h		Quantity of fumigant, mg			
	Wt, g	Thickness, cm	CH_3Br	CH_2CHCN	CH_3Br applied	CH_3Br sorbed	CH_2CHCN applied	CH_2CHCN sorbed
2	500	2	3	5.5	8.4	0	3.6	2.6
5	500	2	2	3	21	1.2	9	7.6
10	500	2	3	3	42	2.6	18	10.3
4	2500	10	2.5	6	16.8	10.5	7.2	7.1
10	2500	10	4	5	42	23	18	17

[a] Average time for fumigant to reach equilibrium above and below commodity.

Table II. Penetration and Sorption of Methyl Bromide and Acrylonitrile in Wheat, Flour, Corn, and Peanuts for 8 h in 6-L Desiccators with 70% Methyl Bromide–30% Acrylonitrile Formulation

Commodity	Dosage, mg/L	Temp, °C	Quantity of commodity		Time to penetrate, h		Sorption quantity, mg	
			Wt, g	Thickness, cm	CH_3Br	CH_2CHCN	CH_3Br	CH_2CHCN
Corn	4	25	2500	10	2	5		
	10	25	2500	10	2	8	12	16
	108	25	2500	10	2	6	225	173
	45	0	2500	10			86	78.5
	108	0	2500	10	1	8	197	189
Peanuts	1.7	25	1000	10	3	3	3	4
	4.2	25	1000	10	0.5	4	11	7.5
	10	25	1000	10	0.5	2	26	18.0
	18	0	1000	10	8	8	45	32.5
	108	0	1000	10	8	1	189	193
Wheat	10	25	2500	10	4	7	23	17
	108	0	500	2	8	8	45	172
	108	0	2500	10	3	8	153	187
Flour	10	25	1000	5	2	6	27	17.4
	10	25	2000	10	2		37	18
	126	0	1000	5	2	8	387	221
	108	0	2000	10	8		400	197

present. The quantity of acrylonitrile dropped to a much greater extent from 18 to 7.7 mg with 500 g of wheat and from 18 to 1 mg with 2500 g. The results in Table I are an average of four separate analyses except for the 2-mg/L treatment which is from two analyses and the 10-mg/L treatment with 500 g of wheat which is an average of 8 analyses. The variability was less than 5% of the amount applied.

The rate of penetration of methyl bromide through a 10-cm layer of material was greatest in peanuts and decreased in corn, flour, and wheat as shown in Table II when a 10-mg/L concentration of the fumigant mixture was applied at 25 °C. At 0 °C and 108-mg/L mixture the order of methyl bromide penetration was corn, wheat, peanuts, and flour. Acrylonitrile at both 25 and 0 °C was generally slower than methyl bromide in penetrating all three seed commodities and it did not penetrate a 10-cm layer of flour by the end of the 8-h exposure. Replacement of the methyl bromide in the fumigant mixture with carbon dioxide did not affect the rate of acrylonitrile penetration into the commodity and no difference was noted when acrylonitrile was used alone.

Data on sorption of methyl bromide by a commodity of 10-cm thickness treated at 25 °C with 10 mg/L of the fumigant mixture showed that flour took up the largest quantity of methyl bromide equal to 18.5 mg/kg, peanuts and wheat about half this amount (10.4 and 9.6 mg/kg, respectively), and corn absorbed the least (4.8 mg/kg). At 0 °C and 108-mg/L mixture, sorption on wheat, corn, and peanuts was somewhat similar for all these commodities with about half the total amount applied being taken up. In the flour nearly all the methyl bromide was absorbed at this temperature. For the acrylonitrile portion of the mixture sorption in all cases was nearly total, and increased with an increase in dosage and decrease in temperature.

Table III. Depletion of Acrylonitrile Residue on Aeration of Wheat, Peanuts, and Corn Treated with 30% Acrylonitrile, 70% Methyl Bromide in 6-L Desiccators for 8 h at 25 °C

Commodity	Dosage, mg/L	Wt of commodity, g	Time after treatment, days	Residue, ppm
Wheat	2	500	0[a]	2.2
	2	500	1	0
Wheat	5	500	0	4
	5	500	1	0.4
	5	500	2	0
Wheat	10	500	0[a]	25
	10	500	1	5
	10	500	3	3
	10	500	7	2
	10	500	14	1
	10	500	21	0
Wheat	10	2500	1	3.5
	10	2500	2	1.3
Peanut seed	10	1000[b]	0[a]	0
Peanut shell	10	1000[b]	0[a]	220
	10	1000[b]	7	0
Corn	10	2500	0[a]	9.7
Corn	10	2500	14	0
	4	2500	0[a]	2.7
			1	0

[a] First analysis for residue made at 15 min after the end of treatment. [b] Total weight of seed and shell (3:1, w/w).

Tests made at intervals after treatment showed that methyl bromide desorbed completely from the commodities in a few hours but acrylonitrile required many days, depending on the conditions used. The time required for desorption of acrylonitrile from the different commodities at 25 °C (Table III) increased as the dosage was

Table IV. Depletion of Acrylonitrile Residue on Aeration of Commodities Treated with 108 mg/L at 30% Acrylonitrile–70% Methyl Bromide in 6-L Desiccators for 8 h at 0 °C

Commodity	Wt of commodity, g	Time after treatment and held at 0 °C, days	Residue, ppm
Wheat	2500	0[a]	66
		1	15
		2	7.3
		3	5.7
		4	4.1
		7	3.8
		14	2.7
		21	2.2
		35	1.5
		42	0.4
Corn	2500	0[a]	55
		1	8.8
		2	8.6
		3	7.2
		7	4.8
		14	2.9
		21	1.8
		28	1.4
		35	0.9
Peanut seed	1000	0[a]	21
		1	10.3
		2	9.2
		3	8.1
		7	5.5
		14	4.1
		21	2
Peanut shell		0[a]	225
		1	86
		2	65
		3	50
		7	23
		14	10.5
		21	0

[a] First analysis of residual made at 30 min after end of treatment.

increased. Desorption was most rapid from peanuts and slowest from wheat. In peanuts treated with the formulation all of the acrylonitrile was sorbed by the shell with none detected on the seed and this had dissipated completely from the shells in 7 days after treatment. In wheat treated with the lower dosages of 2 and 5 mg/L all of the fumigant was desorbed after 2 days. However, when a dosage of 10 mg/L was applied to 500 mg of wheat, residue declined from 25 to 2 ppm in 7 days and was completely desorbed in 21 days after treatment.

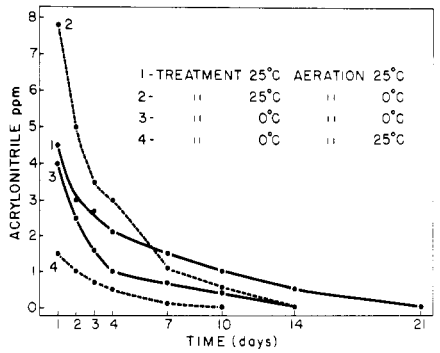

Figure 1. Desorption of acrylonitrile from 500 g of wheat treated with 10 mg/L mixture of 70:30 methyl bromide–acrylonitrile for 8 h in 6-L volume. After 15-min aeration wheat treated at 25 and 0 °C had 20 and 30 ppm, respectively.

The acrylonitrile residue distribution was also determined for the 10-cm layer of commodity by taking one sample from the top 2 and one from the bottom 2 cm. For wheat and corn treated with 45-mg/L mixture for 8 h at 0 °C, after 15-min aeration the top sample had 30% or more acrylonitrile than that at the bottom.

The effect of temperature on rate of desorption of acrylonitrile from wheat treated at 25 and 0 °C is shown in Figure 1. Since methyl bromide was all desorbed in a matter of hours from the commodity no determination on the rate of residue depletion was necessary. In wheat treated at 25 °C the initial residue of acrylonitrile after 15-min aeration was 20 ppm. This wheat was divided into two portions one of which was held at 25 and the other at 0 °C. Desorption was initially faster in the portion held at the higher temperature but because of changes in desorption rate all fumigant was removed in 14 days at 0 °C while 21 days were required for complete desorption at 25 °C. For wheat treated at 0 °C the initial residue at 15 min after treatment was found to be 30 ppm and when this was subsequently divided and aerated at 25 and 0 °C desorption was likewise faster, initially at 25 °C but complete removal of fumigant was reached in 14 days at both temperatures. Although more fumigant was sorbed in the treatment at 0 °C desorption at both 0 and 25 °C was faster than in wheat treated at 25 °C, as if the residue was retained near the surface at the lower temperature. However, it should be noted that in the samples treated at 25 °C and aerated at 0 °C the fumigant was desorbed in the same period of time as in the treatment at 0 °C. Certain components of the wheat, e.g., those previously referred to as being collected in the cold traps of the

Table V. Depletion of Acrylonitrile Residue on Aeration of Wheat Treated in Various Ways to Alter Residue Formation; Fumigation of 500 g with 10 mg/L, 30% Acrylonitrile, and 70% Methyl Bromide in 6-L Desiccators for 8 h at 25 °C

Time, days	Dried at 110 °C before fumigation, h			Dried at 110 °C, 4 h, after fumigation	Dried at 110 °C, 6 h, moisture content reestablished[c]	Flushed with N before fumigation, days		Control
	2	4	6			1	6	
0[a]			15	4[b]	19	26	23	25
1	7.5	4.2	2	2.7	1.8	5.6	2.7	5
2	4	2			1.2		1.7	
3	2.5		0.2		0.7	2.1	1.0	3
4		1		0.8				
5		1				1.8	1.0	3
6	1.5				0.2			
7	1.0	0.5				1.6	0	2.2
14						1.0		0.5

[a] Analysis made after 15-min aeration. [b] This analysis made 4 h and 15 min after the end of fumigation during which time held at 110 °C for 4 h. [c] By storing dried grain in a room with 70% relative humidity.

nitrogen aeration, may be involved in retention at the higher temperature but further work is needed to explain this difference.

In Table IV the desorption of acrylonitrile is given for the treatment and aeration at 0 °C. The desorption time was 42 days for wheat, 35 days for corn, and 21 days for peanuts. Since acrylonitrile desorbed very slowly from wheat treated at 25 °C so that complete desorption required 21 days aeration (Table II) a study was made to find ways of hastening desorption. Wheat was oven dried at 110 °C for 2–6 h before and after treatment with the fumigant to test the effect of removing moisture from the grain and also nitrogen was flushed over wheat prior to treatment to remove any volatile materials that might absorb fumigant (Table V). When wheat was oven dried for 4 h after treatment with the fumigant the desorption time was reduced from 21 to 5 days. If the wheat was dried before fumigation the fumigant desorbed in less than 7 days, and if the dried wheat was stored in a humid atmosphere to reestablish its initial moisture content before fumigation the acrylonitrile was still desorbed in 6 days. This suggested that moisture itself had little influence on retention of acrylonitrile. In this drying procedure in 6 h 12% moisture was removed from the wheat. When wheat was flushed with nitrogen at a flow rate of 50 cm^3/min from 1 to 6 days before fumigation, the desorption time for acrylonitrile was also reduced. Flushing with nitrogen for 1 day, prior to fumigation, reduced the residual acrylonitrile so that only 1 ppm remained after 14-days aeration and when flushing was extended to 6 days no acrylonitrile was present after 7-days aeration.

At the end of 7-days aeration grain was flushed with nitrogen for 1 to 6 days and contained 1.6 and 0 ppm of acrylonitrile, respectively. These amounts are well below the residue in grain, fumigated the same way, but without nitrogen flushing, after aeration at 25 °C.

When passing the nitrogen stream through a cold trap several volatile substances from the grain were found to be condensed in the trap. These were separated into individual components by gas chromatography but they are, as yet, unidentified. The reduced levels of acrylonitrile residue found in wheat subjected to aeration or heat prior to fumigation may have been related to removal of these volatile materials that served to bind the fumigant.

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Determination of Hexabromobenzene in Rat Tissues by Gas–Liquid Chromatography

A method for the determination of hexabromobenzene (HBB) in rat tissues has been evaluated. The recovery from spiked samples is close to 100%. No cleanup procedure is necessary before gas–liquid chromatography on Chromosorb W coated with 4% SE-30 and 6% QF-1 or OV-210. The minimum limit of detection is 0.01 ng of standard HBB and 0.1 ppm of HBB in rat tissues.

Hexabromobenzene (HBB) is a fire retardant used in plastics, textiles, and woods (Negishi et al., 1972; Raley, 1972; Mischutin, 1974; Pashin et al., 1974). Its close relative hexachlorobenzene (HCB) is a fungicide and appears to be ubiquitous (see Vos et al., 1972). Related compounds, polybrominated biphenyls, which are also used as a fire retardant, caused considerable damage in the U.S. dairy and cattle industry (Jackson and Halbert, 1974; Carter, 1976). Another related compound, hexabromobiphenyl, was observed to induce liver porphyria in several avian species (Strik, 1972). We have been studying the effects of HBB in conjunction with HCB on rats. Therefore, before quantitating HBB residues in rat tissues, the HBB analytical procedure was evaluated. The analytical method for pentachloronitrobenzene (PCNB) and its metabolites (Kuchar et al., 1969) was evaluated for HBB and was modified so that a portion of the aqueous homogenate used for enzymatic analysis can be used also for HBB residue determination. The method was also scaled down for economy and ease of handling.

MATERIALS AND METHODS

The tissues were ground with redistilled water in a glass homogenizer to obtain 20% (w/v) homogenate. The aqueous homogenate or distilled water was spiked with an HBB standard in hexane. The solvent was evaporated gently under nitrogen; then the homogenate was mixed thoroughly before extraction.

Three extraction procedures were evaluated. In each extraction, 0.2 ml of homogenate was used. The homogenate was mixed with 5 ml of acetonitrile before adding 5 ml of water. The solution was then shaken with 5 ml of hexane (procedure 1). The homogenate was mixed with 5 ml of water and shaken with 5 ml of hexane (procedure 2) or benzene (procedure 3). The solution was shaken in a test tube with a screw cap lined with Teflon for 0.5 or 1 h on a mechanical shaker (Buchler Instrument). After shaking, the solution was centrifuged and the solvent layer analyzed by gas–liquid chromatography (GLC).

Procedure 1 was used to extract the HBB residue from various tissues of rat pups, which nursed on dams that were fed rat diet containing 80 ppm of HBB.

Analysis of HBB was performed by using a gas–liquid chromatograph equipped with a tritium detector (Aerograph HyFi Model 600). Glass columns 0.4 cm i.d. × 90, 105, and 120 cm long were packed with Chromosorb W (AW) coated with 4% SE-30 + 6% QF-1 (column A) or OV-210 (column B). Unless indicated, the oven was maintained at approximately 195 °C while the nitrogen gas flow was 35 or 50 ml/min depending on the column