

THE RETENTION OF METHALLYL CHLORIDE AND METHYL BROMIDE BY FUMIGATED GRAIN

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I. INTRODUCTION

The use of fumigants against insects attacking stored products involves two possible dangers. In the first place workers may be poisoned by inhaling the fumigant either during its use or its manufacture. Secondly the fumigant may be adsorbed onto food-stuffs thereby hazarding the health of consumers.

In a previous communication (Van Tiel, 1948) the toxicity of the gaseous phase of methallyl chloride and methyl bromide towards white rats was described. The present investigation deals with the retention of these substances by grain during and after fumigation, and the possible toxicity of fumigated grain when used as food.

II. CHEMICAL INVESTIGATIONS

A. *Materials and methods*

Grain was fumigated in a gas chamber of 0.345 m.³ capacity at a temperature of 25° C.

The amount of methallyl chloride necessary to provide the required dosage was evaporated by a stream of air which was led into the fumigating chamber by pressure.

Since methyl bromide is a gas at normal temperatures and pressures its method of application was somewhat different. After opening the tap of a glass cylinder containing the liquid methyl bromide under excess pressure the necessary volume of gas was passed into the fumigating chamber by means of a flow meter and a needle valve.

After fumigation the grain was ventilated by means of a strong current of air. At various times during this ventilation samples of the grain were taken and analysed for their halogen content by the method described by Winteringham and Pieters (Winteringham, 1942; Pieters & Popelier, 1945).

In order to determine the accuracy of the sampling and analytical methods the following experiment was made. Six identical open-necked bottles were filled with grain and placed in the fumigation chamber and fumigated for 24 hr. with methallyl chloride. The chamber was then thoroughly ventilated for 1 hr. and the bottles made gas-tight as quickly as possible one after the other. The entire contents of these bottles were subjected to analysis for halogen content.

Since it was known that during the first few minutes of ventilation the halogen content may fall

very rapidly and a difference of some seconds in taking samples may cause considerable differences in the results, ventilation was continued for 1 hr. before the samples were removed for analysis. On the other hand, this time of ventilation was short enough to leave a sufficient amount of halogen for analysing.

The results of six replicates were 60, 62.5, 55, 57.5 and 52.5 mg. methallyl chloride per kg. of grain, respectively. The average was 57.1 with a standard deviation of ± 3.7 .

Duplicate quantities of 10 kg. grain were fumigated for 24 hr. with methallyl chloride and methyl bromide in concentrations of 80 and 20 g./m.³, respectively, these being the normal concentrations used in practice. After one fumigation the grain was ventilated by forced draught for 2 hr. and then stored under normal conditions. After the other fumigation this forced ventilation was continued for 48 hr., in order to find out how long such treatment is necessary in order to remove all traces of halogen. Halogen determinations were also carried out upon non-treated grain.

B. *Experimental results*

The results of a series of halogen determinations taken at various times after starting the ventilator are given in table 1.

It is shown that immediately after 24 hr. of fumigation with methallyl chloride at a concentration of 80 g./m.³ the grain contains 73–83 mg. of this substance per kg. of grain. During 1 min. the methallyl chloride content of the grain may fall from 83 to 55 mg./kg. of grain, but the subsequent rate of fall is much more gradual.

In the first experiment the grain still contained 3–5 mg. of methallyl chloride per kg. after 2 hr. of intensive ventilation followed by exposure to the air for 6 days. In a second experiment involving continuous ventilation for 48 hr. there was still a residue of 10 mg. methallyl chloride per kg. of grain.

It must be concluded, therefore, that small amounts of methallyl chloride may be retained by the grain for some days after fumigation.

It was found that fumigation with methyl bromide at 20 g./kg. of grain left no residue of bromide in the grain even immediately after thorough ventilation had been started.

The untreated grain showed no halogen content by this method of analysis.

Table 1. *Fumigant content of the grain (mg./kg.)*

Time of sampling since conclusion of fumigation	Grain fumigated 24 hr. with methallyl chloride 80 g./m. ³		Grain fumigated 24 hr. with methyl bromide 20 g./m. ³	
	2 hr. ventilation + 6 days exposure to the air	Continuous ventilation (48 hr.)	2 hr. ventilation + 6 days exposure to the air	Continuous ventilation (48 hr.)
1 min.	83	73	0, 0	0
2 min.	55	—	—	—
0.5 hr.	—	—	0	—
1 hr.	—	68	0	0
4 hr.	—	48	—	—
7 hr.	—	40	—	—
24 hr.	38, 35	28	—	—
31 hr.	—	15	—	—
48 hr.	13, 8	10	—	—
72 hr.	5, 5	—	—	—
144 hr.	5, 3	—	—	—

III. BIOLOGICAL INVESTIGATION

A. *Materials and methods*

In order to determine whether the residues of methallyl chloride found in grain after fumigation constitute a danger to consumers, such grain was used as food for white rats for a period of 6½ weeks.

Treated and non-treated grain was made up into rats' food of the usual composition (ground wheat 60%, skimmed milk powder 30%, fat 8.5%, cod-liver oil 1.35% and salt mixture 0.15%).

The test animals were males of the white rat, *Rattus norvegicus albinus*. The body weight of the test rats and their mortality rate were used as criteria of any deleterious effect of methallyl chloride or methyl bromide residues in food.

5 kg. of grain was fumigated for 24 hr. with methallyl chloride in a concentration of 80 g./m.³, and another batch of the same size was fumigated for 24 hr. with methyl bromide in a concentration of 20 g./m.³. A third batch was completely immersed for 5 min. in liquid methallyl chloride in order to expose the material to a maximum effect of this substance. After being fumigated or immersed, the grain was intensively ventilated for 1 hr. and then left exposed to the air. A fourth batch was left untreated.

During the test period the body weight of the animals was determined three times a week. At the conclusion of this part of the test all rats were fed on normal food and their weight determined for another 3 weeks.

B. *Experimental results*

The average increase in body weight of the four groups of rats after having been fed for 42 days on the four different foods was as follows:

Group 1 (rats fed on food containing wheat previously fumigated with methallyl chloride), 10%.

Group 2 (rats fed on food containing wheat previously immersed in methallyl chloride), 12%.

Group 3 (rats fed on food containing wheat previously fumigated with methyl bromide), 12.5%.

Group 4 (rats fed on untreated food), 14%.

After this part of the test had been concluded (total time 46 days) the rats were fed on non-treated food for 20 days longer (i.e. up to 66 days after the test had been started.) The average percentage increase in weight was again calculated for each group for the total time of 66 days and was as follows: group 1, 15%; group 2, 17%; group 3, 18%; group 4, 17.5%.

Statistical analysis of these results showed that the differences are not significant. The mortality of the test animals and the control animals was 0%.

DISCUSSION

This investigation is a further step in the evaluation of methallyl chloride as a grain fumigant in comparison with methyl bromide.

Previous investigations have shown that the gaseous phase of methallyl chloride is considerably less dangerous to animals than is methyl bromide. It has now been shown that the residues of methallyl chloride remaining in grain cannot be considered as a hazard to the consumers of the fumigated product.

Although the retention of methallyl chloride by grain is undoubtedly higher than that of methyl bromide, premising that both fumigants are used in the practical concentration, the influence of the fumigated product upon the growth of white rats proved to be nil. Even immersion of grain in liquid methallyl chloride for 5 min. did not render the product toxic after being aired. Any residues of this fumigant in the grain may therefore be regarded as harmless in this respect.

Table 2. *Growth of the test rats*

Grain untreated	After a test period of 42 days			After a test period of 46 days + recovery period of 20 days			
	Grain immersed for 5 min. in liquid methallyl chloride	Grain gassed for 24 hr. with 80 g./m. ³ methallyl chloride	Grain gassed for 24 hr. with 20 g./m. ³ methyl bromide	Grain untreated	Grain immersed for 5 min. in liquid methallyl chloride	Grain gassed for 24 hr. with 80 g./m. ³ methallyl chloride	Grain gassed for 24 hr. with 20 g./m. ³ methyl bromide
	Percentage increase in weight						
4.5	10	6	8.5	10.5	11.5	11	10.5
9	10.5	8.5	9	15	13.5	11	12
9.5	10.5	8.5	10	16.5	14.5	11.5	14.5
10.5	11	9	10.5	19.5	16	14	15
11.5	11.5	9.5	11.5	25	16.5	14	18.5
16	12	12.5	12	—	17	19	18.5
16.5	12.5	16.5	14.5	—	17.5	24	20
17.5	13	—	16	—	20	—	22
20.5	14	—	17	—	21	—	24
25	14.5	—	17	—	22	—	24
	Percentage average increase in weight						
14	12	10	12.5	17.5	17	15	18

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