Part 5 Methyl Bromide Gas Penetration, Sorption and Desorption under Disinfestation Standards for Export to The U.S.

Introduction

The following two general quarantine procedures would be used for export apples to the United States; ie. apples in plastic field bins (31.8 cm×63.5 cm×32 cm in size, 0,062 m^3 in capacity) with many vent hales on four sides will be treated by cold storage and then packed in export cartons (38 cm×44.7 cm×25 cm in size, 0,043 m^3 in capacity) with six fiberglass screen-covered vents (4 vents: 2 cm×5 cm, 2 vents: 4 cm×2 cm; vent ratio of 0.74%) at production areas. These apples are then fumigated in quarantine facilities at the port of shipment; apples in plastic field bins will be treated by a combined cold storage and methyl bromide fumigation and then packed in export cartons (38 cm×44.7 cm×25 cm in size, 0,043 m^3 in capacity) without vents in production areas.

On the other hand, it was shown that apple fruit are extremely susceptible to methyl bromide fumigation depending on varieties (PHILLIPS et al., 1939; CLAYPOOL et al., 1956; MORI et al., 1963; MONRO, 1969; O'LOUGHLIN et al., 1977; ABE et al., 1980; RIPPON et al., 1982; GALLETTI et al., 1987; DRAKE et al., 1988; MEHERIUK et al., 1990; DRAKE et al., 1990). Tolerance of 'Fuji' apples to methyl bromide fumigation varied depending on the length of time kept in cold storage prior to fumigation. Apples stored for shorter periods after harvest may show chemical injuries (Part 4, Test 1 in this report).

Methyl bromide gas should reach the fumigation items during fumigation and the gas from removed the items after fumigation as fast as possible when fruit and vegetables are fumigated. Furthermore, it is necessary to know in advance the amount of gas absorbed by fumigation items, and the amount of gas equivalent to the loss must be added to initial dose (MONRO, 1969a; BOND et al., 1984).

Our objectives were to test absorbed ratios of methyl bromide to fumigation items (export cartons, plastic field bins and packing materials); the state of gas penetration into fumigation containers; and gas desorption from fumigated items under export conditions to the United States when they are fumigated with disinfestation standards established for export apples (Part 2, Test 4 in this report).

Test 1 Methyl Bromide Sorption

Materials and Methods

1. Fumigation Items

Fumigation items, such as 'Fuji' apples and each different packing material used for export (carton box, paper mold pack, cardboard sheet, polyethylene mesh sheet and polyethylene fruit cap), were prepared for methyl bromide fumigation with amount of each fumigation material item equivalent to that of 40% loading (v/v).

2. Fumigation

Each fumigation material item was placed in a 29.5 ℓ fiber-glass fumigation chamber (26.0 cm × 28.0 cm × 46.0 cm in size) equipped with circulation fan, ventilation apparatus, and ports for gas application, and sampling, manometer and temperature probe and fumigated at a dose of 30 g/m^3 of methyl bromide for 2 hours at 15°C.

The gas circulation fan was operated continuously during fumigation and gas concentrations were monitored with a gas chromatograph (FID : GC 8AF, Shimazu) at 30 and 120 minutes after injection of the gas. Following fumigation, the chambers were exhausted for 1 hour at 15°C by using the ventilation apparatus.

Results

Results of the tests are shown in Table 5-1. Sorption ratio of methyl bromide were 9.7%, 5.3%, 3.7% and 0.7 to 1.3%, respectively, for carton boxes, polyethylene fruit caps, apples, cardboard sheets, polyethylene mesh sheets, and paper mold packs. It was determined that methyl bromide was absorbed mainly by the carton boxes and polyethylene fruit caps and that initial doses of 19.4 to 20.0% were absorbed to all fumigation items during fumigation.

Table 5-1. Methyl bromide concentrations recorded in a 29.5 ℓ fiber-glass chamber containing fumigation material items. Fumigation at a dose of 30 g/m^3 for 2 hours at 15°C with 40% loading.

Fumigation items	Gas concentration (mg/ℓ)		Percent sorption
	30	120 min.	
Carton boxes	27.2	27.1	9.7
Paper mold packs	29.8	29.6	1.3
Polyethylene mesh sheets	29.8	29.6	1.3
Cardboard sheets	29.7	29.8	0.7
Polyethylene fruit caps	28.5	28.4	5.3
'Fuji' apples	31.8	28.9	3.7

Test 2 Methyl Bromide Gas Sorption, Penetration and Desorption in Practical Fumigation

Materials and Methods

1. Fruit Packing and Fruit Containers for Fumigation

Export Carton Boxes

The export carton is 0.043 m^3 (38 cm×44 cm×25 cm in size) with a total vent ratio of 56 cm^2 (4 vents: 2 cm×5 cm in size, 2 vents: 4 cm×2 cm in size; vent ratio of 0.74%) on four sides. Each apple was covered with a meshed polyethylene fruit cap and placed on a polyvinyl molded pack. Fruit was then packed in the export carton (36 fruit, ca. 10 kg) in two layers. One macerated paper sheet was placed on the bottom of the carton and between the first and second layer, and one polyethylene meshed sheet was placed on the top of the first layer. Export cartons were sealed with sealing tape and stored at 15°C before fumigation.

Plastic Field Bins

A 0.062 m^3 plastic field bin (31.8 cm×63.5 cm×32 cm in size) with many vent holes on four sides was used for fumigation. Seventy to 80 fruit (ca. 20 kg) were placed in this bin without packing materials and stored at 10°C before fumigation.

2. Methyl Bromide Fumigation Standards

Standard 1: 38 g/m^3 of methyl bromide for 2 hours at 15°C with 40% loading, fruit packed in export cartons.

Standard 2: 48 g/m^3 of methyl bromide for 2 hours at 10°C with 50% loading, fruit placed in plastic field bins

3. Fumigation

To make a load of 40% or 50%, five export cartons (ca. 50 kg) or four plastic bins (ca. 80 kg) were placed in a 0.52 m^3 stainless steel fumigation chamber (0.9 m×0.66 m×0.86 m in size) equipped with 0.86 m^3/min. circulation fan and ventilation apparatus, graduated dispenser, ampoule breaker and vaporizer for methyl bromide application, ports for gas sampling, temperature probe and manometer as used in the large-scale mortality tests.

Fumigation was conducted at 15°C or 10°C for 2 hours. Methyl bromide enclosed in ampoules was applied by using the built-in ampoule breaker. The built-in circulation apparatus was kept on for the first 30 minutes, and then an automatic timer was used (on: 0.5 minutes, off: 2.5 minutes) throughout the fumigation.

Teflon tubes (internal diameter of 4 mm) for monitoring gas concentration were installed in an open space in the fumigation chamber and at the center of the carton box and the plastic field bin.

Gas concentrations were monitored by using a gas chromatograph (FID: GC 8AF,

Shimazu) at 10, 30 and 120 minutes after injection of the gas. Air temperatures within the chamber and fruit pulp temperature were monitored with a multi-channel automatic temperature recorder (Hybrid Recorder: AH, Chino).

Following fumigation, the chamber boxes were exhausted for one hour at 15°C by using the built-in ventilation apparatus.

4. Storage of Fumigated Fruit and Monitoring Methyl Bromide

Fumigated fruit and export cartons for methyl bromide sorption tests were stored under conditions simulating commercial transport to the United States; ie. in the case of Standard 1, fumigated fruit were stored for 24 hours (minimum period) at ambient temperature (ca. 15°C) in the fumigation chamber and then for 24 hours (minimum period) at 0°C in a cold chamber. In the case of Standard 2, fumigated fruit removed from plastic field bins and packed in export cartons without vents were stored for 48 hours at 10°C and then stored for 48 hours (minimum period) at 0°C in a cold chamber. They were then stored for 48 hours (minimum period) at 0°C in a cold chamber for commercial transport to the United States from Japan.

Fruit packed in export cartons were taken periodically from storage rooms and put back in the aforementioned 0.52 m^3 fumigation chamber with the amount equivalent to a maximum loading of 60% (v/v) for the shipping container and stored for 24 hours at 15°C or 10°C to accelerate the desorption of methyl bromide from fruit and export cartons. Methyl bromide concentrations were monitored by using a gas chromatograph (FID).

Results and Discussion

1. Methyl Bromide Sorption and its Penetration

The result of these sorption and penetration tests are shown in Table 5-2. The ratios of residual gas to initial doses of methyl bromide were 80.3% to 80.9%, and approximately 20% of the initial doses was absorbed to export cartons. This result coincided with that from Test 1. It could be said that methyl bromide was absorbed mainly by carton boxes and polyethylene fruit caps. The ratios in plastic field bins were rather high with 100.6% to 102.0%. No methyl bromide was absorbed to plastic field bins and a relatively small amount of methyl bromide was sorbed by the apples. Gas concentrations inside both export cartons and plastic bins reached uniformity after 10 minutes regardless of doses. The gas penetrated satisfactorily into carton boxes with a vent ratio of 0.74% and into plastic field bins with many vent holes. Gas concentrations during exhaust were 1.1 to 1.2 mg/ℓ in 10 minutes in export cartons and 0.2 mg/ℓ in 5 minutes in plastic field bins. It could be said that both fruit containers were suited for methyl bromide fumigation.

Table 5-2. Gas concentrations in a 0.52 m^3 fumigation chamber containing export cartons and plastic field bins. Fumigation at 33.8 to 34.0 g/m^3 for 2 hours at 15°C with 40% loading and at 24.7 to 46.7 g/m^3 for 2 hours at 10°C with 50% loading.

Fumigation items	Replicate	Temperature (°C)	Dose (g/m^3)	Gas sampling point	Gas concentration (mg/ℓ)			Percent residual gas
					10	30	120 min.	
Empty chamber	1	15	33.8	air space	33.5	34.4	33.3	98.5
Empty export carton (containing packing materials, fruit)	1	15	34.0	air space	—	29.4	27.3	80.3
	2	15	34.0	air space	—	29.3	27.5	80.9
Export carton (containing fruit)	1	15	34.0	air space	33.9	32.2	28.5	83.8
				in carton	31.2	31.4	28.1	82.6
	2	15	33.8	air space	33.7	32.1	28.6	84.6
				in carton	32.4	31.5	28.0	82.8
Empty plastic field bin	1	10	46.7	air space	—	48.4	47.0	100.6
	2	10	24.7	air space	—	25.2	25.2	102.0
Field bin (containing fruit)	1	10	39.1	air space	44.0	43.2	38.7	99.0
				in bin	43.5	43.5	38.5	98.5

Table 5-3. Methyl bromide concentrations desorbed from 'Fuji' apples and export cartons fumigated with Standard 1 (38 g/m^3 of methyl bromide for 2 hours at 15°C with 40% loading) and stored under conditions simulating commercial transport to the United States for Japan.

Gas sampling point	Methyl bromide gas concentration (ppm)					
	Storage at 15°C		Storage at 0°C			
	1	2 day	1	2	3	4 day
air space in fumigation chamber	36.3	8.0	—	1.3	—	ND
in export carton	36.0	7.7	—	1.3	—	ND

2. Methyl Bromide Desorption

Methyl bromide concentrations monitored periodically during storage under conditions of commercial transport are shown in Table 5-3 (Standard 1) and Table 5-4 (Standard 2).

Results of the tests showed that gas concentrations between air space in fumigation chamber and in export cartons were not different and reached the 1 ppm level after 3 to 4 days in storage at 0°C.

Absorbed methyl bromide will desorb gradually from fruit and export cartons and diffuse inside and outside of the cartons. As a result, both gas concentrations in the air space in fumigation chamber and in cartons will be equivalent.

From these test data, no methyl bromide would be detected from apple fruit or export cartons when unloaded at ports of entry in the United States.

Table 5-4. Methyl bromide concentration desorbed from 'Fuji' apples and export cartons fumigated with Standard 2 (48 g/m³ of methyl bromide for 2 hours at 10°C with 50 % loading) and stored under conditions simulating commercial transport to the United States for Japan.

Gas sampling Point	Methyl bromide gas concentration (ppm)							
	Storage at 10°C		Storage at 0°C					
	1	2 day	1	2	3	4	5	6 day
air space in fumigation chamber	62.3	23.8	—	4.4	—	1.7	—	ND
in export carton	62.3	24.6	—	4.6	—	1.4	—	ND