Part 6 Residue Analysis for Organic Methyl Bromide and Inorganic Bromide in Fumigated Apples

Introduction

If chemical reaction takes place between the gas and the materials, new compounds are formed. An example is the appearance of inorganic bromide compounds after treatment of some foodstuffs with methyl bromide (MONRO, 1969b). Methyl bromide also remains in foodstuffs for a short term. Permissible residue tolerances for apple fruit fumigated with methyl bromide are ND and 5 ppm, respectively, for methyl bromide and inorganic bromide in the United States (Environmental Protection Agency, 1989). Hence, residues of organic methyl bromide and inorganic bromide were determined for 'Fuji' apples treated by the combined cold storage and methyl bromide fumigation treatment (Part 2, Test 4 in this report) established and stored under conditions of simulating commercial export to the United States.

Materials and Methods

1. Test Fruit

Medium size (36 per box) 'Bagged Fuji' and 'Unbagged Fuji' apples were obtained from a packing house in Hirosaki City, Aomori Prefecture and then stored at 1°C for 40 days prior to fumigation.

2. Disinfestation Standards and Fruit Packing

Standard 1: Cold storage (Standard Cold storage at 0.5±0.5°C for 40 days or more, fruit in plastic field bins) +Methyl bromide fumigation (Methyl bromide at 38 g/m^3 for 2 hours at 15°C or above with 40% or less loading, fruit packed in export cartons).

Each apple was covered with a polyethylene fruit cap and were placed with two layers 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 in size; vent ratio of 0.74%). One macerated paper sheet was placed on the bottom of the carton and between the first and the second layers, and one polyethylene meshed sheet was placed on the top of the first layer, respectively. The export carton (36 fruit, ca. 10 kg) was sealed with sealing tape and stored at 15°C before fumigation.

Standard 2: Cold storage (Standard Cold storage at 0.5±0.5°C for 40 days or more, fruit in plastic field bins) +Methyl bromide fumigation (Methyl bromide at 48 g/m^3 for 2 hours at 10°C or above with 50% or less loading, fruit in plastic field bins).

Seventy to 80 fruit (ca. 20 kg) were placed in 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 and then stored at 10°C before fumigation.

3. Fumigation

To make a load of 40% and 50%, five export cartons (ca. 50 kg) and four plastic field bins (ca. 80 kg) were placed in a 0.52 m^3 of 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 test.

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.

Methyl bromide concentrations were monitored with a gas chromatograph (FID : GC 8AF, Shimazu) after 30 and 120 minutes of exposure. Air and fruit temperatures during fumigation were monitored with a multi-channel automatic temperature recorder (Hybrid Recorder : AH, Chino). Following fumigation, the air-fumigant mixture was exhausted for one hour at 15°C or 10°C by using the built-in ventilation apparatus.

4. Storage of Fumigated Fruit

Fumigated fruit for organic methyl bromide analysis were stored under conditions simulating commercial transport to the United States ; ie. in the case of Standard 1, fruit were stored for 24 hours (minimum period) at 15°C before loading in shipping container and then for 14 days at 0°C (transportation period and temperature). In the case of Standard 2, fruit were packed in export cartons without vents (38 cm × 44.7 cm × 25 cm in size, 0.043 m^3 in capacity). They were stored for 48 hours (minimum period) at 10°C before loading into shipping container and then placed for 14 days at 0°C (transportation period and temperature). Fruit for inorganic bromide analysis were packed in export cartons and stored at 0°C for 7 days prior to residue analysis.

5. Analytical Methods

Organic Methyl Bromide

Two apples were taken at random from each storage lot which was stored for a given period of time. The same manner was used to take for control samples. The analysis for organic methyl bromide was conducted periodically (1, 4, 6, 9, 12, 13 and 14 days in Standard 1 ; 1, 2, 4, 6, 9, 13 and 14 days in Standard 2) using the method described by KING et al. (1981).

Our analytical procedures were almost the same as described in technical reports on organic methyl bromide residues in nectarines, cherries and apples for Japan from the United States. Each sample consisted of 50 g from the whole apple which was placed in 100 mℓ of distilled water in a 360 mℓ Eberbach blender jar. The samples were homogenized for 3 minutes and then allowed to equilibrate for 20 minutes at 30°C. A 20 mℓ of the headspace over the apple pulp was injected into a gas chromatograph (ECD) equipped with a gas sampling valve and a GSQ megabore capillary column (30 m × 0.53 mm ID). The detection limit was 0.001 ppm. Standards of known methyl bromide concentrations were prepared by the addition of measured volumes of methyl bromide gas (1 to 0.001 ppm) to

unfumigated apples in the blender jar.

Inorganic Bromide

Inorganic bromide residues in fruit were determined using a bromide ion-selective electrode (Orion 960 Auto chemistry system, Orion, USA).

The serial calibration technique was applied for the analysis (Orion Research Incorporated, 1982 ; GNANASUNDERAM et al., (1983) ; ie. the electrodes were immersed in a solution, which was composed of 1 mℓ of 5N-KNO_3 to 5 mℓ of distilled water in the beaker at 25° C. A set amount of 0.0005N-NaBr of a standard solution was added to the same beaker with stirring. The relationship between the bromide residues (ppm) and the electrode potential (mV) was analyzed automatically by the Orion 960.

Fruit pulp removed free of the core portion was placed in a beaker and homogenized as the sample for the analysis. The liquid was then centrifuged at 2,000 rpm for 15 minutes. The supernatant was decanted into a 50 mℓ beaker to which 1 mℓ of 5N-NaBr was added at 25°C. The electrodes were placed in the solution with stirring and bromide residues (ppm) were determined. The analysis was conducted in 3 to 9 replicates. In the recovery test, standards of known NaBr concentration were prepared by the addition to samples made of unfumigated apples in a beaker and determined by the Orion 960 as described in above. The recoveries of NaBr added to samples were 98.4% in 1.6 ppm, 94.8% in 4.1 ppm and 92.5% in 8.2 ppm.

Results

1. Organic Methyl Bromide

Methyl bromide gas concentrations during fumigation were shown in Table 6-1. The average of residual gas concentrations 2 hours after fumigation were 34.5 mg/ℓ and 48.5 mg/ℓ for Standard 1 and Standard 2.

Organic methyl bromide residue levels are shown in Table 6-2. These data showed that organic methyl bromide residues in fumigated apples with Standard 1 and Standard 2 declined rapidly to less than 0.001 ppm in 12 to 14 days and 13 to 14 days after fumigation, respectively. These data show that organic methyl bromide in apples would be less than 1 ppb when unloaded at ports of entry in the United States.

Table 6-1. Methyl bromide concentrations for 'Fuji' apples fumigated with methyl bromide at 38 g/m³ for 2 hours at 15°C with 40% loading (Standard 1) and at 48 g/m³ for 2 hours at 10°C with 50% loading (Standard 2).

Standard	Replicate	Methyl bromide concentration (mg/ℓ)		
		15	60	120 min.
Standard 1*	1	37.8	—	34.7
	2	38.5	35.2	34.3
Standard 2**	1	58.1	53.1	49.9
	2	54.8	52.7	47.1

* Fruit packed in export cartons were fumigated.
** Fruit placed in plastic field bins were fumigated.

Table 6-2. Organic methyl bromide residues in 'Fuji' apples fumigated with methyl bromide at 38 g/m³ for 2 hours at 15°C with 40% loading (Standard 1) and at 48 g/m³ for 2 hours at 10°C with 50% loading (Standard 2).

Standard	Replicate	Organic methyl bromide residue (ppm±SD*)							
		1	2	4	6	9	12	13	14 days
Standard 1	1	0.75 ±0.02	—	0.012 ±0.002	0.005 ±0.0005	0.0034 ±0.0006	—	0.0014 ±0.0003	<0.001
	2	—	—	—	—	—	<0.001	<0.001	—
Standard 2	1	—	1.26 ±0.104	—	0.019 ±0.0054	0.0034 ±0.002		0.0013 ±0.0002	<0.001
	2	2.58 ±0.23	—	0.024 ±0.016	—	—	—	<0.001	<0.001

* Standard deviation.

2. Inorganic Bromide

Inorganic bromide levels in fumigated apples are shown in Table 6-3. The residue revels were 2.6 ppm (applied dose of 34.4 g/m³) and 2.8 to 4.2 ppm (applied dose of 44.4 to 48.9 g/m³), respectively, for Standard 1 and Standard 2. The level in unfumigated control apples was 0.2 to 0.4 ppm. This residue level was below the U.S. accepted tolerance of 5 ppm.

Table 6-3. Inorganic bromide residues in "Bagged Fuji' and 'Unbagged Fuji' apples fumigated with methyl bromide at 34.4 g/m³ for 2 hours at 15°C with 41% loading (Standard 1) and 44.4 to 48.9 g/m³ for 2 hours at 10°C with 50% loading (Standard 2).

Fruit	Methyl bromide doses (g/m³)	Fumigation temperature (°C)	Gas concentration (mg/ℓ) 30 min.	120 min.	Inorganic bromide residues (ppm±SD*)
Bagged Fuji**	34.4	15	31.8	28.9	2.56±0.34
	44.4	10	48.4	44.3	3.28±0.98
	48.9	10	56.0	50.9	4.21±0.65
	Cont.	—	—	—	0.17±0.09
Unbagged Fuji***	44.4	10	48.4	44.3	2.82±0.53
	Cont.	—	—	—	0.42±0.14

* Standard deviation.
** 'Bagged Fuji' was cultivated with paper bag.
*** 'Unbagged Fuji' was cultivated without paper bag.