RES. BULL. PL. PROT. JAPAN No. 34 : 1～10 (1998)

Methyl Bromide Sorption in Fruit Varieties

Fusao KAWAKAMI, Takashi MISUMI, Tetsuo OOGITA,
Masahiro TANNO and Yukihiro SOMA

Chemical & Physical Control Laboratory, Research Division, Yokohama Plant Protection Station 1-16-10, Shinyamashita, Naka-Ku, Yokohama 231-0801, Japan

Abstract : Relationship between CT product and varietal characteristics was tested with 3 nectarine varieties and 13 apple varieties. Each variety was fumigated with methyl bromide at a dose of 48 g/m³ for 2 hours at 20°C with 0.143 kg/l loading (nectarines) and 56 g/m³ for 2 hours at 10°C with 0.16 kg/l loading (apples). The gas decline patterns indicated physical sorption (adsorption) took place at the initial stage of fumigation in nectarines, while gas penetration coincided with gas absorption during fumigation in apples. The CT products were a 66.0 g・h/m³ and a 71.0 g・h/m³ for 'Shuhou' and 'Fantasia' nectarines and the difference may be attributable to Shuhou's larger surface area. No significant differences in apple varieties were observed on the CT products by size in 'Mutsu' and 'Fuji', while significant differences were observed among 'Mutsu' (121.8 g・h/m³), 'Sekaiichi' (116.4 g・h/m³)='Fuji' (115.4 g・h/m³) and Alps Otome' (106.1 g・h/m³). These differences were not attributable to the size factor. The CT products from similar size in 12 varieties showed significant differences were observed in varieties. Especially a large difference was observed on 'Tsugaru' (106.3 g・h/m³) and 'Mutsu' (118.1 g・h/m³) and the difference may be attributed to Tsugaru's smooth and oily skin and soft pulp. The factor affecting the CT product was not specified in apples. The different CT products, however, were obviously attributed to varietal characteristics. It is considered that some factors may mutually take part in the action of methyl bromide.

Key words : methyl bromide, fumigation, gas sorption, CT product, varietal characteristics, nectarines, apples

Introduction

Many different factors can be affected the toxicity of fumigants to a given species of the pests. MONRO (1969), FAO (1983), and CHAKRABARTI (1996) described that the effectiveness of a fumigant is determined by the amount of gas in air and its penetrating powers. A most important factor affecting the action of methyl bromide is the phenomenon known as sorption covered three types of phenomena of absorption, chemisorption and adsorption. The sorption of a gas involves both physical and chemical process and the sorption is the uptake or retention of the gas in a commodity that takes place during fumigation. The sorptive values of materials vary according to their density and porosity and physical sorption is an extremely important factor affecting the successful outcome of fumigation.

YOKOYAMA *et al.* (1987) reported the LD50's of codling moth eggs on 'Summer Grand' cultivars of nectarines were significantly more susceptible than the eggs on other cultivars 'May Grand', 'Firebrite', 'Red Diamond', 'Spring Red' and 'Fantasia'. Many flaws such as very fine skin cracks on 'Summer Grand' may have contributed to the difference in egg mortality by methyl bromide/fruit interaction. KING & BENSCHOTER (1991) also reported at any dose tested methyl bromide residues were greater in oranges and tangerines than in grapefruit and the fruit surface area to volume ratio was a possible major factor in the amount of methyl bromide absorbed. MAINDONALD *et al.* (1992) found differences in sorption of methyl bromide among cherry varieties.

These reports indicate that the different sorption of methyl bromide in fruit varieties depends on fruit or its characteristics, and that the amount of methyl bromide sorbed is an important factor in the determination of disinfestation standard.

Our objectives were to test gas sorption and CT product of methyl bromide to Japanese nectarine and apple varieties.

Materials and Methods

Test Fruit

Nectarines

Three late season varieties of 'Fantasia', 'Flavortop' and 'Shuhou' were obtained from local packinghouses in Fukushima Prefecture at the end of August in 1997. The fruit were stored for 5 days at 5°C and then placed in the fumigation room for 24 hours at 20°C of fumigation temperature before testing.

Apples

Thirteen varieties were used for the test. The fruit were harvested in October to November in 1997 and then stored at 0°C. 'Alps Otome' from Nagano Prefecture, 'Indo' from Hokkaido, and 'Mutsu', 'Jonagold', 'Fuji', 'Oorin', 'Sekaiichi', 'Jonathan', 'Hokuto', 'Kinsei', 'Starking Delicious', 'Sensyu' and 'Tsugaru' from Aomori Prefecture were obtained from local packinghouses, respectively. The fruit were stored for a few days at 2°C and then placed in the fumigation room for 24 hours at 10°C of fumigation temperature before testing.

Each variety of nectarines and apples was weighed by top-loading digital balance (LIBROR EB-3200D, Shimadzu) with special attention to be adjusted fruit loading of 0.143 kg/*l* (nectarines) and 0.16 kg/*l* (apples).

Fumigation

A 29.5-liter fiber-glass fumigation chamber (26.0 cm × 28.0 cm × 41.0 cm) was used for fumigation. The chamber was equipped with a circulation fan, ventilation apparatus, gas application and sampling ports, a manometer and temperature probes.

The fruit were placed in the fumigation chamber by variety and then fumigated with methyl bromide at a dose of 48 g/m^3 for 2 hours at 20°C (nectarines) and 56 g/m^3 for 2 hours at 10°C (apples). The circulation fan was used throughout fumigation. Gas concentrations were monitored with gas chromatograph (GC-8AIF with FID, Shimadzu) at 10, 30, 60, 90 and 120 minutes after injection of methyl bromide. Following fumigation, all chambers were exhausted for one hour at fumigation temperatures. The fumigation were conducted two to three replicates.

Measurement of Fruit and Data Analysis

After fumigation, specific gravity, firmness and sugar content were measured on 5 fruits from each variety to examine the relationship between CT product and varietal characteristics. The firmness of two places of nectarines and 5 places of apples was measured with a fruit hardness tester (KM type, Fujiwara). The sugar content was measured with a temperature-compensated digital refractometer (DX-55, Atago). The specific gravity of fruit was determined by replacing water with fruit.

The rate (%) of residual gas concentrations was calculated based on the gas concentrations (mg/*l*) in 10 minutes and 2 hours after injection of methyl bromide. Concentration times time (CT) products were calculated similarly to the method described by Monro (1969). Significant difference for CT product was analyzed by Tukey's multiple range test ($\alpha = 0.05$).

Results and Discussion

Nectarines

Fig. 1 shows means of gas concentrations for 3 varieties monitored periodically in two to three fumigation. The progressive gas concentrations showed with the lowest level in 'Shuhou' and the highest level in 'Fantasia'. The differences were observed in 10 minutes after injection of methyl bromide and almost similar differences were maintained till the end of fumigation. The gas decline patterns indicate that the phenomenon of physical sorption (adsorption) took place at the initial stage of fumigation.

Table 1 shows residual gas rate, gas sorption and CT product. There was little difference of the CT product in each replicate in each variety. Significant difference was observed on the CT product between 'Shuhou' and 'Fantasia'. The CT products were a 66.0 g • h/m^3 and a 71.0 g • h/m^3 for 'Shuhou' and 'Fantasia', respectively and the difference was a 7%.

Table 2 shows fruit weight, specific gravity, firmness, sugar content and fruit characteristics. The firmness of 'Fantasia' and 'Shuhou' was harder than that of 'Flavortop', no correlation, however, was estimated between the fruit firmness and the CT product.

The results showed 'Shuhou' was the highest methyl bromide sorbed variety among

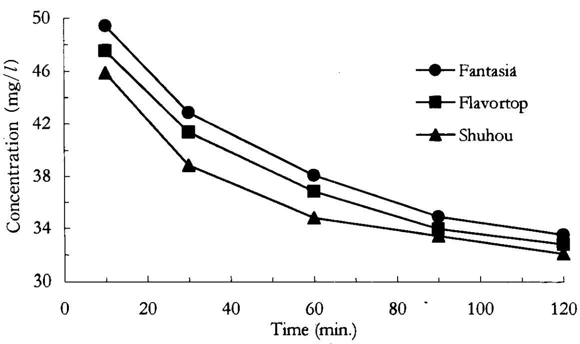


Fig. 1. Progressive gas concentrations for 3 nectarine varieties fumigated with methyl bromide at a dose of 48 g/m^3 for 2 hours at 20°C with 0.143 kg/*l* loading in a 29.5-liter fumigation chamber.

Table 1. Residual gas rate, gas sorption and CT product for 3 nectarine varieties fumigated with methyl bromide at a dose of 48 g/m^3 for 2 hours at 20°C with 0.143 kg/l loading in a 29.5-liter fumigation chamber.

Varieties	Replicate	No. of fruit (fruit/rep.)	Residual gas rate (%±SD)	Gas sorption (mg/kg±SD)	CT product* (g•h/m3±SD)
Fantasia	1	32	68.2	133.1	71.1
	2	32	67.1	139.8	69.9
	3	32	68.4	134.2	72.0
	mean	32	67.9±0.69	135.7±3.59	71.0±1.08 a
Flavortop	1	26	69.7	136.2	69.8
	2	26	68.4	141.9	67.8
	mean	26	69.1±0.91	139.0±3.98	68.8±1.42 ab
Shuhou	1	30	69.7	146.7	66.1
	2	30	70.3	144.9	65.9
	mean	30	70.0±0.41	145.8±1.25	66.0±0.18 b

*The same letter are not significantly different by Tukey's multiple range test (P>0.05).

Table 2. Fruit weight, specific gravity, firmness, sugar content and fruit characteristic of 3 nectarine varieties fumigated with methyl bromide at a dose of 48 g/m^3 for 2 hours at 20°C with 0.143 kg/l loading in a 29.5-liter fumigation chamber.

Varieties	Weight (g/fruit)	Specific gravity (kg/l)	Firmness (kg)	Sugar content (Brix%)	Fruit characteristics
Fantasia	132	0.97	2.8	12.5	smooth skin
Flavortop	162	1.00	1.3	10.5	smooth skin
Shuhou	140	0.93	2.6	10.0	rough skin

three varieties. The varietal difference may be attributable to Shuhou's larger surface area as 'Shuhou' has relatively rough skin compared to smooth skin of other two varieties.

Apples

1. Relationship Between Fruit Size and CT Product

Fig. 2 shows means gas concentrations for 4 varieties monitored periodically in three fumigations.

The progressive gas concentrations showed with small differences in 10 minutes after injection of methyl bromide and with gradually larger differences at the lapse of exposure time. The gas decline patterns indicate that the phenomena of gas penetration and gas absorption took place at the same time during fumigation.

Table 3 shows fruit weight, residual gas rate, gas sorption and CT product. There was little difference of the CT product in each replicate in each variety. No significant difference was observed on the CT product by the sizes in 'Mutsu' and 'Fuji'. Significant

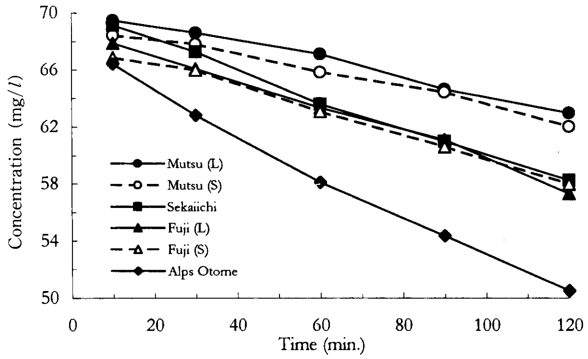


Fig. 2. Progressive gas concentrations for 4 apple varieties fumigated with methyl bromide at a dose of 56 g/m^3 for 2 hours at 10°C with 0.16 kg/l loading in a 29.5-liter fumigation chamber.

Table 3. Fruit weight, residual gas rate, gas sorption and CT product for 4 apple varieties fumigated with methyl bromide at a dose of 56 g/m^3 for 2 hours at 10°C with 0.16 kg/l loading in a 29.5-liter fumigation chamber.

Varieties	No. of fruit	Weight	Residual gas rate	Gas sorption	CT product*
	(fruit/rep.)	(g/fruit)	(%±SD)	(mg/kg±SD)	(g·h/m^3±SD)
Mutsu (L)	9	527	90.7±1.42	34.2±2.73	121.8±1.43 a
Mutsu (S)	19	249	90.7±3.43	38.9±5.78	120.3±1.42 a
Sekaiichi	7	674	84.3±2.38	60.7±6.88	116.4±1.07 b
Fuji (L)	10	472	84.5±1.81	60.8±3.89	115.4±0.76 b
Fuji (S)	21	225	86.7±2.19	55.1±4.69	115.0±0.89 b
Alps Otome	202**	23	76.0±2.06	95.2±5.97	106.1±1.54 c

*The same letter are not significantly different by Tukey's multiple range test ($P>0.05$).
**No. of fruit were 189, 222 and 195 for 1st, 2nd and 3rd replicate, respectively.

differences, however, were observed among 'Mutsu' (121.8 g • h/m^3), 'Sekaiichi' (116.4 g • h/m^3)='Fuji' (115.4 g • h/m^3) and 'Alps Otome' (106.1 g • h/m^3), respectively. The difference between 'Mutsu' and 'Alps Otome was a 13%. Especially, the difference of the CT product between 'Alps Otome' (23 g/fruit) and 'Sekaiichi' (674 g/fruit) was smaller than that between 'Alps Otome' and 'Mutsu' (527 g/fruit) although surface area to volume of 'Sekaiichi' was smaller than that of 'Mutsu'.

The results indicated that the differences of the CT product among varieties were not attributable to the size factor, and that the difference between 'Alps Otome' and 'Sekaiichi' may be caused by Alps Otome's higher rate of surface area of calyx to volume and quick gas penetration and gas absorption to fruit.

2. Relationship between Varietal Characteristics and CT Product

Fig. 3 shows means of gas concentrations for 12 varieties monitored periodically in two to three fumigations. The progressive gas concentrations showed with the lowest level in

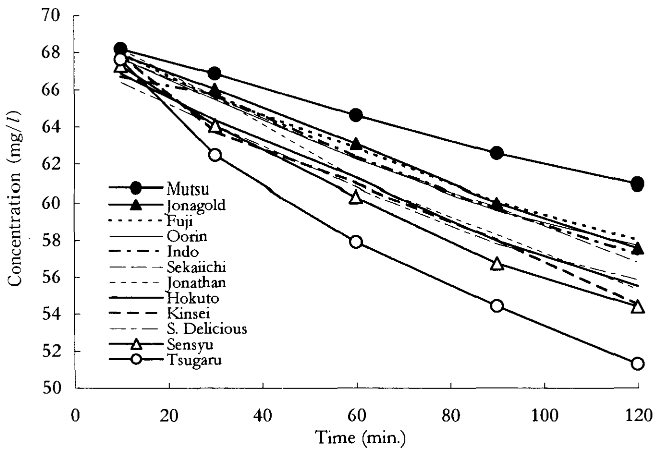


Fig. 3. Progressive gas concentrations for 12 apple varieties fumigated with methyl bromide at a dose of 56 g/m³ for 2 hours at 10°C with 0.16 kg/*l* loading in a 29.5-liter fumigation chamber.

Table 4. Fruit weight, specific gravity, firmness, sugar content and fruit characteristic of 12 apple varieties fumigated with methyl bromide at a dose of 56 g/m³ for 2 hours at 10°C with 0.16 kg/*l* loading in a 29.5-liter fumigation chamber.

Varieties	Weight (g/fruit)	Specific gravity (kg/*l*)	Firmness (kg)	Sugar content (Brix%)	Fruit characteristics*
Mutsu	337	0.82	2.5	10.7	thick & smooth skin
Jonagold	337	0.78	2.0	13.1	smooth & oily skin
Fuji	344	0.87	2.5	14.0	water core
Oorin	337	0.83	2.6	13.0	rough skin
Indo	165	0.85	3.0	14.9	hard pulp
Sekaiichi	363	0.80	2.5	12.4	soft pulp
Jonathan	278	0.77	2.3	13.3	smooth skin
Hokuto	337	0.85	2.4	12.6	thick skin, water core
S. Delicious	337	0.85	2.4	13.6	water core
Kinsei	363	0.84	2.5	13.1	rough skin
Sensyu	337	0.84	2.3	12.6	thick & oily skin
Tsugaru	295	0.78	1.9	12.2	smooth & oily skin, soft pulp

*Bull. Fruit Tree Res. Stn., Japan.

'Tsugaru' and the highest level in 'Mutsu', respectively. The gas decline patterns were almost the same as shown in Fig. 2.

Table 4 shows fruit weight, specific gravity, firmness, sugar content and fruit characteristics of 12 varieties. Table 5 also shows residual gas rate, gas sorption and CT product. Little difference of the CT product was observed in each replicate in each variety.

No correlation was observed between the specific gravity, the firmness and sugar content and the CT product. Significant differences were observed in the CT product

Table 5. Residual gas rate, gas sorption and CT product for 12 apple varieties fumigated with methyl bromide at a dose of 56 g/m³ for 2 hours at 10°C with 0.16 kg/*l* loading in a 29.5-liter fumigation chamber.

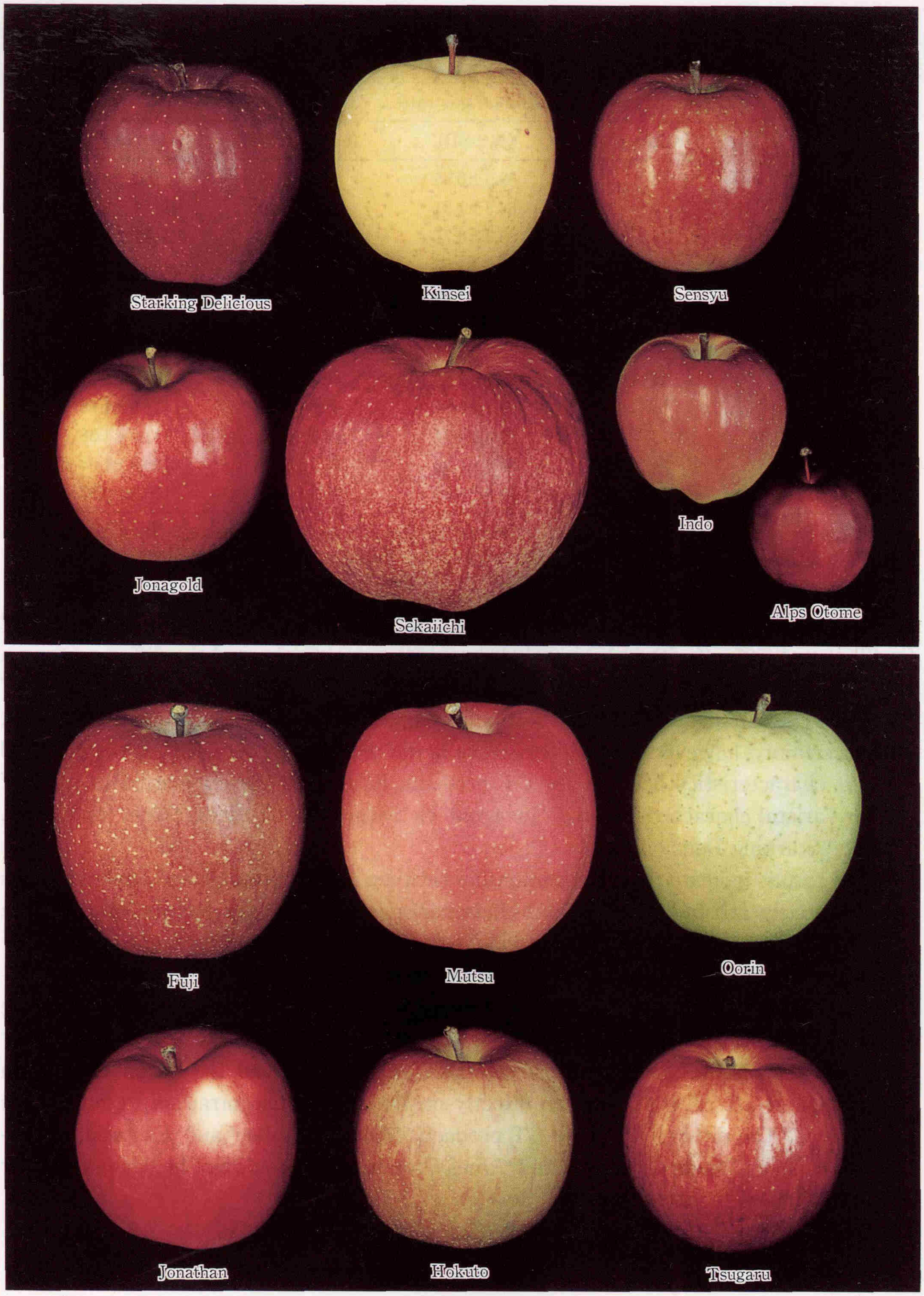
Varieties	No. of fruit	Residual gas rate	Gas sorption	CT product*
	(fruit/rep.)	(%±SD)	(mg/kg±SD)	(g•h/m³±SD)
Mutsu	14	89.5±0.55	43.2±2.89	118.1±0.32 a
Jonagold	14	84.8±1.31	64.0±3.90	114.8±0.35 ab
Fuji	14	85.3±0.71	54.3±2.50	114.6±0.53 ab
Oorin	14	85.3±1.65	58.7±3.56	113.9±1.07 bc
Indo	29**	85.8±1.50	59.6±4.82	113.9±0.82 bc
Sekaiichi	13	83.9±2.61	66.0±5.20	113.9±1.04 bc
Jonathan	17	83.2±2.39	69.2±0.14	113.4±0.72 bcd
Hokuto	14	83.1±2.07	68.2±3.62	111.5±0.27 bcd
S. Delicious	14	84.1±0.62	66.6±1.69	111.0±1.06 cd
Kinsei	13	80.3±0.74	74.1±2.83	111.0±1.38 cd
Sensyu	14	80.8±1.95	74.7±5.26	110.0±1.04 d
Tsugaru	16	75.8±0.85	95.2±1.92	106.3±0.97 e

*The same letter are not significantly different by Tukey's multiple range test ($P>0.05$).
**No. of fruit were 28, 28 and 30 for 1st, 2nd and 3rd replicate, respectively.

between or among varieties. The CT products were a 106.3 g • h/m³ and a 118.1 g • h/m³ for 'Tsugaru' (295 g/fruit) and 'Mutsu' (337 g/fruit), respectively and the difference was a 10%. The difference between two varieties may be attributed to fruit characteristics of Tsugaru's smooth and oily skin and soft pulp compared to Mutsu's thick and smooth skin. The uncertainty, however, was still existence in the relationship between gas sorption and varietal characteristics because the CT products from each variety varied in spite of similar varietal characteristics, e.g. 'Jonagold' vs 'Sensyu' vs 'Tsugaru', Oorin' vs 'Kinsei', 'Fuji' vs 'Starking Delicious'.

The results indicate that the relationship between methyl bromide and apple varieties were obviously attributed to varietal characteristics although the factors affecting the different CT products were not specified in the test. It is considered that some factors may mutually take part in the action of methyl bromide.

The mortality effect against the egg stage, which is most tolerant to methyl bromide fumigation, of the codling moth (GAUNCE *et al.*, 1980 ; TEBBETS *et al.*, 1986 ; WADDELL *et al.*, 1989), the oriental fruit moth (YOKOYAMA *et al.*, 1987) and the peach fruit moth (KAWAKAMI *et al.*, 1994) depends on directly on the actual concentration present during fumigation. The differences of the CT products between 'Shuhou' and 'Fantasia' nectarines and among 'Tsugaru', 'Mutsu' and 'Alpus Otome' apples could not be disregarded for obtaining higher efficacy of the treatment.



Japanese apple varieties used for the test.

References Cited

CHAKRABARTI, B. (1996) Methyl bromide in Storage Practice and Quarantine. (The Methyl Bromide Issue. (BELL, C.H. ; N. PRICE and B. CHAKRABARTI eds.), Chichester:John Wiley & Sons. 243.

FAO (1983) International plant quarantine treatment manual. FAO Plant Prod. Prot. Paper **50** : 10-11.

GAUNCE, A.P., H.F. MADSON, R.D. MCMULLEN and J.W. HALL (1980) Dosage response of codling moth stages to fumigation with methyl bromide. Can. Ent. **112** : 1033-1038.

KAWAKAMI, F., S. MOTOSHIMA, K. KUROKAWA *et al.* (1994) Plant Quarantine Treatment of 'Fuji' Apples for Export to The United States. Res. Bull. Pl. Prot. Japan 30, No 2 : 1-80.

KING, J.R. and C.A. BENSCHOTER (1991) Comparative Methyl Bromide Residues in Florida Citrus : A Basis for Proposing Quarantine Treatments against the Caribbean Fruit Fly. J. Agric. Food Chem. **39** : 1307-1309.

MAINDONALD, J.H., B.C. WADDELL and D.B. BIRTLES (1992) Response to Methyl Bromide Fumigation of Codling Moth (Lepidoptera : Tortricidae) Eggs on Cherries. J. Econ. Entmol. **85** : 1222-1230.

MONRO, H.A.U. (1969) Manual of fumigation for insect control. FAO Agri. stud. 14-18, 25-30.

TEBBETS, J.S., P.S. HARTSELL and H.D. NELSON (1986) Dose/response of codling moth (Lepidoptera : Tortricidae) eggs and nondiapausing and diapausing larvae to fumigation with methyl bromide. J. Econ. Entmol. **79** : 1039-1043.

WADDELL, B.C., D.B. BIRTLES and P.R. DENTENER (1989) Methyl bromide fumigation for the control of codling moth (Lepidoptera : Tortricidae) on different cherry and nectarine cultivars : a cultivar comparison tests. Managing Postharvest Horticulture in Australia New Agriculture & Fisheries. pp. 157-165.

YOKOYAMA, V.Y., G.T. MILLER and P.L. HARTSELL (1987a) Methyl Bromide Fumigation for Quarantine Control of Codling Moth (Lepidoptera : Tortricidae) on Nectarines. J. Econ. Entomol. **80** : 840-842.

YOKOYAMA, V.Y., G.T. MILLER and P.L. HARTSELL (1987b) Methyl Bromide Fumigation for Control the oriental Fruit Moth (Lepidoptera : Tortricidae) in nectarines. J. Econ. Entomol. **80** : 1226-1228.

和 文 摘 要

果実品種間における臭化メチルの収着性

川上　房男・三角　　隆・扇田　哲男
丹野　昌浩・相馬　幸博
横浜植物防疫所調査研究部消毒技術開発担当

日本産ネクタリン3品種を臭化メチル 48 g/m³, 2時間, 20°C, 収容比 0.143 kg/*l* の基準で，りんご13品種を臭化メチル 56 g/m³, 2時間, 10°C, 収容比 0.16 kg/*l* の基準でそれぞれくん蒸し，果実の品種とCT値の関係について調査した。ネクタリンでは，“ファンタジア”が 71.0 g・h/m³ で最も大きく，最も小さい“秀峰”(66.0 g・h/m³) との間に7%の差が認められた。“秀峰”はくん蒸初期の段階でガス濃度が低く，“秀峰”の果皮が粗く表面積が大きい特性が物理的収着（吸着）を大きくした原因と考えられる。りんごでは，異なるサイズの調査で“陸奥”(121.8 g・h/m³), “世界一”(116.4 g・h/m³) 及び“ふじ”(115.4 g・h/m³) と“アルプス乙女”(106.1 g・h/m³) の間に有意差が認められたが，同一品種内ではサイズの違いによる差が認められず，サイズがCT値の差に影響を与えていないことが示唆された。同じサイズの12品種を用いた調査では各品種間で有意差が認められたが，要因を特定するまでには至らず，複数の要因が相互に関与していることが考えられた。品種のうち“津軽”(106.3 g・h/m³) と“陸奥”(118.1 g・h/m³) の間には10%の差が認められた。これは，“津軽”の特性である果皮表面が滑らかで，油脂分を多く含み，果肉が柔らかい性質が，ガスの収着量を増加させたことが考えられる。