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Vapormate® as a Quarantine Fumigant for Orange Treatment

Bo Kyung Sung[1], Min Goo Park[1], Robert Ryan[2], Yonglin Ren[3], ByungHo Lee[4*] and Tae Joon Kim[4]

Abstract: In Korea, 10% methyl bromide (MB) has been used to the imported oranges for QPS (Quarantine and Pre-Shipment) purpose, and amount of the consumption of MB was reached to 82t in 2007. Mandatory fumigation with MB was carried out for treatment of imported oranges (96.7% of total) in order to meet National Plant Quarantine Service (NPQS) requirement. Although MB use for soil fumigation has been decreased by year to year due to the ozone depletion issue, its use for QPS fumigation is increasing continuously because of increasing of global trades and protection of agro-ecosystem in imported counties against quarantine pest. Currently, as one of the potential alternatives, ethyl formate is considered to use for treatment of postharvest commodities. A cylinder formulation of 16.7% ethyl formate, named Vapormate, was developed by the Linde Group for fumigation of durable commodity. To extend the application purposes, the Linde Group and Dongbu HiTek have tested Vapormate for perishable commodity fumigation, especially for imported and exported fruits. This study was conducted to obtain the more systematic data to control different stages of two spotted mites (*Tetranychus urticae* Koch) and citrus mealybugs (*Planococcus citri* (Rossi)) in terms of estimated CT product. The L(CT)$_{99}$ values of ethyl formate were 96 and 21 g·h/m^3 against eggs of two spotted mites and adults of citrus mealybugs at 21 ±2℃, respectively. In a semi-field test with Vapormate on oranges, the completed control of mites and mealybugs were achieved at 210 g/m^3 for 4hr at both 5℃ and 17 ±2℃. In the post fumigation, the quality (loss of firmness, color change and total soluble solid) for 1, 6 and 15 days at 6℃ storage was not significantly different. The final residue of applied ethyl formate was detected at the level of 0.042 ppm that is under the Maximum Residue Limits (MRLs) for dried fruits in Australia. Vapormate could play an important role to reduce MB use and to protect ozone layer as a MB replacement for QPS treatment purposes.

Introduction

In Korea, 10% methyl bromide (MB) has been used to treat the imported oranges for Quarantine and Pre-Shipment (QPS) purpose, and amount of the consumption of MB was reached to 82t in 2007. Mandatory fumigation with MB was carried out for treatment of imported oranges (96.7% of total) in order to meet National Plant Quarantine Service (NPQS) requirement. Although MB use for soil fumigation has been decreased by year to year due to the ozone depletion issue, its use for QPS fumigation is increasing continuously because of increasing of global trades and protection of agro-ecosystem in imported counties against quarantine pest. Currently, as one of the potential alternatives, ethyl formate is considered to use for treatment of postharvest commodities. A cylinder formulation of 16.7% ethyl formate, named Vapormate®, was developed by the Linde Group for fumigation of durable commodity. To extend the application purposes, the Linde Group and Dongbu HiTek have tested Vapormate® for perishable commodity fumigation, especially for imported and exported fruits. In this paper, we report more systematic data regarding with use of Vapormate® to control different stages of two spotted mites (*Tetranychus urticae* Koch) and citrus mealybugs (*Planococcus citri* (Rossi)) in laboratory test and semi-field conditions. Also, assessment of the quality and residue were evaluated post fumigation.

Materials and Method

Fumigant Bioassays

A different stages of two spotted mites (*Tetranychus urticae* Koch) and citrus mealybugs (*Planococcus citri* (Rossi)) were used to predict L(CT99) values. The Ethyl formate fumigation was conducted for 4hr at 21 2℃ in 8L gas-tight glass desiccators. After 4 hr fumiga-

1. *NPQS, South Korea*
2. *The Linde Group*
3. *CSIRO Entomology, GPO Box* 1700, *ACT* 2601, *Canberra, Australia.*
4. *Dongbu ARI, Dongbu HiTek, South Korea*
* *byungholee@ dongbu. com*

tion, the desiccators were opened and aerated in the fume hood for 2hr. Mortality of adult and nymph was assessed under a microscope at 24hr post fumigation. In case of *T. urticae*, hatching rate of eggs was investigated after incubation for 4 – 5 days.

Fruit Quality Assessment

Navel oranges imported from Australia and California were used for quality assessment. Vapormate at 210 and 420 g/m^3 applied for 4hr at both 5 and 17℃ in 0.5m^3 stainless steel fumigation chambers filled with 25% of orange. After 4 hr exposure, the chambers were opened and aerated for 2hr using fan and then the commodity was stored at 6 2℃. The quality (loss of firmness, color change, total soluble solid and pitting or pericarp browning and fungal decay) were accessed for 1, 6 and 15 days at 6℃ storage

Residue Analysis

The oranges were fumigated with 50 g/m^3 of ethyl formate for 24hr at 21 2℃ in 6L gastight glass desiccators and then aerated for 3hr. For residue analysis, all samples were analyzed by a solvent extraction method as described by Vu and Ren (2004)[1].

Results and Discussions

The efficacy of ethyl formate for different stages of two spotted mites (*T. urticae*) and citrus mealybugs (*P. citri*) is shown Table1. The LC values are useful fundamental data for future practical trials because dose of ethyl formate in fumigation chamber is variable depending on sorption of target fresh fruits, loading factors and their application methods (formulated with CO_2) as well as fumigation conditions. The estimated $L(Ct)_{99}$ values of ethyl formate were 96 and 21g · h/m^3 against eggs of two spotted mites and adult citrus mealybugs, respectively.

Table 1. Toxicity of ethyl formate to two spotted mites and citrus mealybugs.

Species	Stage	LC_{50} (mg/L)	LC_{95} (mg/L)	LC_{99} (mg/L)	Slope (SE)[a]	DF	x^2
T. urticae	Adult	4.96	7.39	8.71	9.51 (±1.1)	23	2.56
	Egg	12.68	36.82	55.95	3.63 (±1.3)	23	15.43
P. citri	Adult	5.19	8.25	10.00	8.18 (±1.5)	23	2.84
	Nymph	2.89	5.58	7.34	5.77 (±1.4)	26	5.46

[a]Standard error

There were no found in significant quality differences between the fumigated orange (Vapormate 210 and 420 g/m^3) and untreated one in terms of firmness, pitting or pericarp browning, fungal decay, or total soluble solids for the 1st and 6th day of storage (Table 2 and Table 3). A slight pitting on surface of orange fumigated at 420 g/m^3 of Vapormate at 17℃ was investigated in 15th day of storage.

Table 2. Phytotoxic effect of Vapormate to orange fumigated for 4hr at 17℃ (15th day storage at 6 ± 1℃)

Vapormate concentration (g/m^3)	Pitting ± SD a	Firmness ± SD (kg or N)	Fungal decay ± SD b	Soluble solids ± SD (%)
0	0.40 ± 0.50 abc	0.83 ± 0.01	1.00 ± 0.00	10.67 ± 0.74
210	0.20 ± 0.41 a	0.82 ± 0.03	1.00 ± 0.00	10.67 ± 0.55
420	1.25 ± 0.55 c	0.83 ± 0.05	1.00 ± 0.00	10.93 ± 0.15
Significance (*P*)	0.000	0.963	1.000	0.790

Table 3. Phytotoxic effect of Vapormate to orange fumigated for 4hr at 5℃ (15th day storage at 6 ± 1℃)

Vapormate concentration (g/m^3)	Pitting ± SD a	Firmness ± SD (kg or N)	Fungal decay ± SD b	Soluble solids ± SD (%)
0	1.00 ± 0.72 ac	0.79 ± 0.02	1.10 ± 0.32	12.07 ± 2.01
210	1.25 ± 0.67 a, b	0.79 ± 0.03	1.00 ± 0.00	12.55 ± 1.50
420	1.40 ± 0.55 b	0.80 ± 0.02	1.00 ± 0.00	12.63 ± 1.59
Significance (*P*)	0.023	0.197	0.381	0.734

[a] Damage score: 0 (none), 1 (slight), 2 (moderate), 3 (severe).
[b] Decay score: 1 (none), 2 (25%), 3 (50%), 4 (75%), 5 (entire fruit)
[c] Means in a column followed by the same letter are not significantly different at the 5% level.

The partitioning of ethyl formate between air and the salts in spiking sample system is shown in Figure 1. Equilibrium partition between air and each salt was examined within 20min. Ethyl formate was stable in the headspace over either sodium sulfate plus orange or sodium sulfite plus orange. Ethyl formate in the headspace of ammonium nitrate and zinc sulfate wasn't even detected at 1 min. The final residue of ethyl formate exposed to 50 g/m^3 for 24h at 21 ± 2℃ and aerated for 3hr was detected at the level of 0.042 ppm.

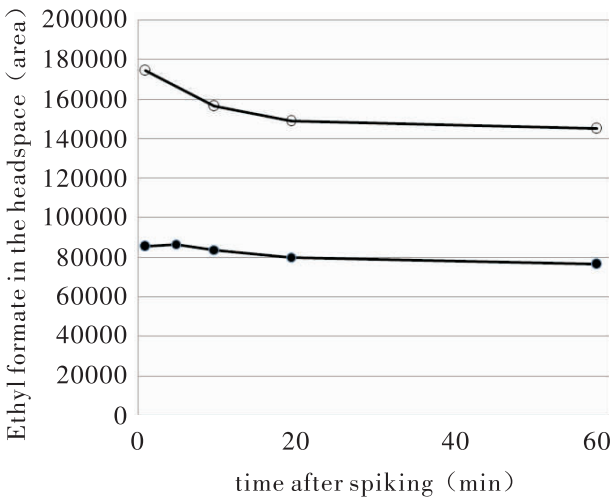

Fig. 1 Amount of ethyl formate in the headspace above spiked standards of orange in – ○ – sodium sulfate, – ● – sodium sulfite.

The L(CT)$_{99}$ values of ethyl formate were 96 and 21 g · h/m^3 against eggs of two spotted mites and adults of citrus mealybugs at 21 ± 2℃, respectively. In a semi – field test with Vapormate on oranges, the completed control of mites and mealybugs were achieved at 210 g/m^3 for 4hr at both 5℃ and 17 ± 2℃. In comparison with untreated oranges, the quality (loss of firmness, color change and total soluble solid) of treated oranges have not significan different or changes for 1, 6 and 15 days storage at 6℃. The final residue of ethyl formate was detected at the level of 0.042 ppm which is below the Maximum Residue Limits (MRLs) for dried fruits in Australia.

Vapormate® could play an important role to reduce MB use and to protect ozone layer as a MB replacement for QPS treatment purposes.

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