0709

Efficacy of Sulfuryl Fluoride on Stored Grain Pests in a Warehouse Trial in China

Zeng Ling*, Zhang Xinfu, Xian Qing and Chen Jiadong

Abstract: Sulfuryl Fluoride is widely applied and is considered as a feasible substitute for methyl bromide in many countries. Efficacy of sulfuryl fluoride on stored grain pests, including *R. dominica*, *S. oryzae*, *and T. castaneum*, in a warehouse trial were undertaken in Guangzhou City of Guangdong Province, China in May 2006. According to the trial results, the doses of 40 – 5 g/m^3 with 48h – 7d exposures gave complete mortality of adults, larvae and pupae of insect species, but couldn't complete control eggs. After exposed to sulfuryl fluoride 30 – 40 g/m^3 for 48 h, the sulfuryl fluoride residues in paddy, flour, wheat, milk, rice were below the maximum levels in food premises. It is concluded that sulfuryl fluoride is an effective fumigant for control stored grain pests in China. These results will support sulfuryl fluoride product for registration.

Key words: sulfuryl fluoride, fumigation, stored grain pests

Introduction

Lesser grain borer *Rhzopertha dominic* (Fabricius), rice weevil *Sitophilus oryzae* (Linnaeus) and red flour beetle *Tribolium castaneum* (Herbst) are three important stored grain pest species. They can cause reduction in weight and quality of stored grain [1]. At present, the control of stored grain pests are largely relied on the use of chemical insecticides, especially fumigants. Methyl bromide (MB) as a fumigant permitted for use in grain and dry food products, has been widely used for half a century [2]. However, the use of methyl bromide is being phased-out due to its ozone-depleting properties [3,4]. Under the Montreal Protocol, methyl bromide is being phased out in developed countries and developing countries by 2005 and 2015[5]. Therefore, there is an urgent need for suitable alternatives to replace methyl bromide.

A lot of studies showed that sulfuryl fluoride (SO_2F_2) has been potential to control a wide variety of postharvest pests[6-9], including quarantine pests[10,11]. It could be a good candidate, as it can be utilized under almost the same conditions as MB, particularly with regard to its exposure time[12,13]. This fumigant has been registered for structural fumigations against termites, wood boring beetles and pantry pests for nearly 40 years[14]. Sulfuryl fluoride, presently marketed under the trade name ProFume®, has now been registered for insect pest control in food commodities and food processing facilities in the USA and in some countries in Europe[15-20].

In China, sulfuryl fluoride has been used to fumigate a variety of buildings and non-edible commodities[21-23], but has not been used in food premises until the end of 2007. Efficacy of sulfuryl fluoride on stored grain pests, including *R. dominica*, *S. oryzae*, and *T. castaneum*, in a warehouse trial were undertaken in Guangzhou City of Guangdong Province, China in May 2006. The results presented in this paper from upper trial carried out according to the method to meet the registration requirements of Institute for the Control of Agrochemicals, Ministry of Agriculture (ICAMA), China. ICAMA is the national authority responsible for pesticide registration and supervision. Using these results, the efficacy data from several other research laboratories, Shandong Longkou Chemical Factory will submit its sulfuryl fluoride product for registration in the ICAMA utilising dosages based on the target species, lift stage.

Materials and Method

Insect Pests

Species tested had included *R. dominica*, *S. oryzae*, and *T. castaneum*. *R. dominica* and *S. oryzae were reared on whole wheat*, *T. castaneum* was reared on a 3∶3∶1 mixture of broken wheat, rolled oats and yeast. The cultures were maintained at 25 ± 1℃ and 70% – 80% r. h. From these cultures, adults of three species (1

Guangdong Institute for Cereal Science Research
No. 222 North Yuexiu Road, Guangzhou, Guangdong, 510050, *P. R. China* [* *zengl@ tom. com*]

-2 weeks old) were taken for preparation of mixed-age cultures. About 300 adults of *R. dominica*, *S. oryzae*, and *T. castaneum* were released separately into 200g of their respective rearing media in glass jars, and cultured them for 60 days to make that there were adults, eggs, larvae and pupae in each jar. Rearing media containing mixed-age cultures of the insects were weighed in 50g into cloth bags (20cm, 15cm size) and the bags were placed individually in the warehouse. In each fumigated warehouse, three cloth insect bags was hanged at upper point, middle point and lower point separately for each specie as three replicates for each dose of sulfuryl fluoride + CO_2 mixtures, with an equal number (three) of untreated control replicates

Fumigation

Fumigations were carried out in six small warehouses which were the same size. The size of each warehouse was: length × width × height $= 6m \times 3.5m \times 3m = 63m^3$.

Sealing was undertaken to improve the warehouses fumigant gas retention properties. All of doors and windows were mainly sealed with polyethylene sheeting and double sealed them with sealing adhesive, newspaper and paste. Performed sealing of door after introduction tube well placed.

The fumigant sulfuryl fluoride (99.8%, produced and provided by Shandong Longkou Chemical Factory) was contained as a pressurised liquid in steel cylingders. The cylingders, which remained outside the fumigated warehouses when in use, were connected using a short length of copper tubing fitted with rubber tubing that could be closed by pinch clamp. Sulfuryl fluoride and CO_2 were taken separately from two compressed gas cylingder into the same application mixing bottle, then injected sulfuryl fluoride + CO_2 mixtures in the bottle into the test warehouse with a 1cm outside diameter and 0.7cm inside diameter polyethylene tube (introduction tube). Fixed one end of the introduction tube in the middle of the warehouse, the other end was introduced to the outside of the warehouse through sealed door and connected with application mixing bottle to perform introduction. The application mixing bottle was a 5 000mL aspirator bottle for distilled water. The quantity of sulfuryl fluoride to be introduced was calculated according to the intended dose. The dosage of CO_2 was calculated on the basis of $100g/m^3$ of the warehouse volume.

Mixed-age cultures of different insect species were exposed to sulfuryl fluoride + CO_2 mixtures for 48hours ($40g/m^3 + 100g/m^3$ and $30g/m^3 + 100g/m^3$, active ingredient, the same below) and 7 days ($10g/m^3 + 100g/m^3$ and $5g/m^3 + 100g/m^3$). A reference fumigation was carried out. This was with 56% aluminium phosphide tablets, produced by Henan Zhengzhou Pesticide Factory, at $3.36\ g/m^3$ (active ingredient; the dosage of tablet was $6g/m^3$). Controls were placed in another warehouse at the same temperature.

Observations on Mortality

Following fumigation respectively, the test insect bags were taken out. The contents of the bags were transferred to individual glass jars (250mL size) and maintained at 27℃ and 70% r. h. in the laboratory at the Guangdong Institute for Cereal Science Research, for mortality assessments, which were completed after 7 days and 60 days. Rearing media inspection was carried out by cutting open the whole wheat. Counts of live and dead insects were made according to species. The efficacy was evaluated according to the formula below:

$$\text{Mortality}(\%) = \frac{\text{The number of dead insects}}{\text{Test insects}} \times 100$$

$$\text{Corrected mortality}(\%) = \frac{\text{Mortality of the treated} - \text{Mortality of the control}}{100 - \text{Mortality of the control}} \times 100$$

Determination of Residues

At the same place as the cloth insect bags, three cloth bags (25cm, 20cm size) with one of kinds of foods, including paddy, flour, wheat, milk powder and rice bought in market or supermarket, were hanged separately at the upper point, middle point and lower point in each fumigated warehouse as three replicates, each bag of food was about 500g.

At the end of fumigations, the fumigated warehouses were taken outdoors and opened to enable the fumigant to escape. 24 hours later, the residues of sulfuryl fluoride in different fumigated foods were determinated by GC external reference method in accordance with Chemical Reagent General Rules for the Gas Chromatography (GB/T9722-1988)[24].

Results

Temperature

Data on temperatures for the outside of the warehouse during fumigated treatment are presented in Table 1. The target temperature of 25℃ was attained.

Table 1. Average, minimum, and maximum temperatures for all fumigations treatments during the exposure time

℃	1st day	2nd day	3th day	4rd day	5th day	6th day	7th day
Average	26	25	25	25	24.5	24.5	25
Minimum	23	22.5	23	24	22	23	24
Maximum	27	27	25.5	25	24.5	25	25.5

Efficacy

The efficacy of sulfuryl fluoride on adults of tested insect species was shown in Table 2. The result showed that doses of 40 – 5 g/m^3 with 48hours – 7days exposures gave complete mortality of all adults. Rearing media inspection was carried out by cutting open the whole wheat, no live larvae and pupae were found in all fumigation treatments. Following fumigation, for efficacy assessments on eggs, which were completed after 60 days by counting of live adults of insect species. Average number of adults of insect species after 60 days was given in Table 3. The result revealed that doses of 30 – 40 g/m^3 with 48hours exposures were completely control eggs of *R. dominica* and *S. oryzae*, but tested doses couldn't complete control eggs of *T. castaneum*.

Table 2. Efficacy of sulfuryl fluoride on the adults of insect species

Dosage (g/m^3)		Exposure time	Repeated times	Corrected mortality %		
				R. dominica	*S. oryzae*	*T. castaneum*
SO_2F_2	40	48h	3	100	100	100
	30	48h	3	100	100	100
	10	7d	3	100	100	100
	5	7d	3	100	100	100
PH_3	3.36	7d	3	100	100	100
Control			3	0.2**	1.1**	0.33**

Note: Average mortality of Control.

Table 3. Average number of adults of tested insect species after 60 days

Dosage (g/m^3)		Exposure time	Repeated times	Average number of adults		
				R. dominica	*S. oryzae*	*T. castaneum*
SO_2F_2	40	48h	3	0	0	38.3
	30	48h	3	0	0	58
	10	7d	3	0	1	37
	5	7d	3	0.3	1.3	39.7
PH_3	3.36	7d	3	0	0	0
Control			3	21	39.3	>300

The residues of sulfuryl fluoride in different foods

Foods were exposed to sulfuryl fluoride 30 – 40 g/m^3 for 48 h. After 24h of the end of fumigation, the sulfuryl fluoride residues in paddy, flour, wheat, milk, rice were showed in Table 4. According to Maximum Levels of Contaminants in Foods (GB2762 – 2005)[25], the maximum levels of sulfuryl fluoride were 1.0 mg/kg for rice and flour, 1.5 mg/kg for others. Table 4 showed the residues of tested foods were below 1.0 mg/kg which were lower than the maximum levels in food premises.

Table 4. Residues of Sulfuryl Fluoride after Fumigation in Foods

Samples	Sulfuryl fluoride fumigant dose (mg/kg)	
	40 g/m^3	30 g/m^3
paddy	<1.0	<1.0
flour	<1.0	<1.0
wheat	<1.0	<1.0
milk	<1.0	<1.0
rice	<1.0	<1.0

Conclusion and Discussion

According to the trial results, the doses of 40 – 5 g/m^3 with 48h – 7d exposures gave complete mortality of adults, larvae and pupae of insect species. The doses of 30 – 40 g/m^3 with 48hours exposures were completely control eggs of *R. dominica* and *S. oryzae*, but the doses of 40 – 5 g/m^3 with 48h – 7d exposures couldn't complete control eggs of *T. castaneum*. After exposed to sulfuryl fluoride 30 – 40 g/m^3 for 48 h. the sulfuryl fluoride residues in paddy, flour, wheat, milk, rice were below the maximum levels in food premises. It is concluded that sulfuryl fluoride is an effective fumigant for control stored grain insects in China.

The fumigation dosage of sulfuryl fluoride that can control the eggs effectively in the field warehouse is still to be further study.

As a high-performance pesticide, when using, we should perform sealing of fumigation grain mass and grain warehouse carefully to improve airtightness and to enhance the pest control effect. Moreover, sulfuryl fluoride belongs to the toxic gas, during operation, we should pay e-

nough attention to the safety problems, and operators should be trained before operation.

Acknowledgements

The authors thank Prof. Xu Guogan, who was once a researcher of the Plant Quarantine Institute of Ministry of Agriculture, for technical support. Thank Shandong Longkou Chemical Factory for providing sulfuryl fluoride gas cylingder.

References

[1] Bai X G. Stored product insect pests and their control. Beijing: Science Press, 2002: 3

[2] Ren Y L. Philosophy guiding current and future fumigant research. Proceedings of the 8th International Working Conference on Stored-Product Protection, York, UK, 2002: 553 – 555

[3] Shaaya E, Kostjukovski M, Demchenko N. Alternative fumigants for the control of stored-product insects. Proceedings of the 8th International Working Conference on Stored-Product Protection, York, UK, 2002: 556 – 560

[4] UNEP (United Nations Environment Programme). Report of the Methyl Bromide Technical Options Committee, Assessment of alternatives to Methyl Bromide. UNEP, Nairobi, ISBN92 – 807 – 1730 – 8, 1998

[5] Wang Y J. Methyl bromide and its alternative technology (1). Plant Quarantine, 1998, 12(2): 103 – 106. (In Chinese)

[6] Bell C H, Savvidon N. The toxicity of Vikane® (sulfuryl fluoride) to age groups of eggs of the Mediterranean flour moth (Ephestia kuehniella). Journal of Stored Product Research, 1999, 35: 233 – 247

[7] Welker J, Rowley J, Hindes D. Update on the development of sulfuryl fluoride as an alternative to methyl bromide. 2000 annual International Research Conference on Methyl Bromide Alternatives and Emissions Reductions, Orlando, F1orida, USA. 2000, 85: 1 – 85

[8] Zhen J N, Zhou L P, Qiu J L. The development of sulfuryl fluoride applied to fumigation of food. Chinese Journal of Hygienic Inecticides & Equipments, 2005, 11 (2): 115 – 118. (In Chinese)

[9] Xu G G, Jiang S J. The development of sulfuryl fluoride in China and Study on Controlling Stored Grain Pest. Grain & Oil storage technology communications, 2006, 2: 39 – 43. (In Chinese)

[10] Zettler J L, Leesch J G, Gill R F et al. Chemical alternatives for methyl bromide and phosphine treatments for dried fruits and nut. Proceedings of the 7th International Working Conference on Stored-Product Protection, Beijing, Sichuan Publishing House of Science & Technology, 1999, 1: 554 – 561

[11] Zettler J L, Arthur F H. Chemical control of stored product insects with fumigants ans residual treatments. Crop Protection, 2000, 19: 577 – 582

[12] Schneider, B. M. Characteristics and global potential of the insecticidal fumigant, sulfuryl fluoride. Proceedings of the 1st International Conference on Insect Pests in the Urban Environment, Cambridge, UK, 1993: 193 – 198

[13] Schneider B, Hartsell P. Control of stored product pests with Vikane gas fumigation. Proceedings of the 7th International Working Conference on Stored-Product Protection, Beijing, Sichuan Publishing House of Science & Technology, 1999, 1: 406 – 408

[14] Stewart D. Sulfuryl fluoride a new fumigant for control of the drywood termite, *Kalotermes minor* Hagen. Journal of Economic Entomology, 1956, 82: 156 – 158

[15] Thoms E M, Scheffrahn R H. Control of pests by fumigation with sulfuryl fluoride. Dow to earth, 1994, 49(2): 23 – 30

[16] Bell C H, Drinkall M J. Sulfuryl fluoride to replace methyl bromideuse in the flour milling industry. 2000 annual international research conference on methyl bromide alternatives and emissions reductions, Orlando, Florida, 2000, Nov, 6 – 9

[17] Drinkall M J, Zaffagnini V, Suss L, et a1. Efficacy of sulfuryl fluoride on stored product insects in a semolina mill trial in Italy. Proceedings of the 8th International Working Conference on Stored-Product Protection, York, UK, 2003: 884 – 887

[18] Ducom P, Dupuis S, Stefanini V et a1. Sulfuryl fluoride as a new fumigant for the disinfestation of flour mills in France. Proceedings of the 8th International Working Conference on Stored – Product Protection, York, UK, 2003: 900 – 903

[19] Emily B. Searching for options. World Grain, 2003, 4: 67 – 71

[20] Drinkall M J. Development of ProFume (Sulfuryl fluoride) in use in flour mills in Europe. 2003 annual international research conference on methyl bromide alternatives and emissions reductions, San Diego, 2003, Nov. 3 – 6

[21] Li W C. Structural fumigation using Sulfuryl Fluoride, Zhejiang Chemical Industry, 2001, (1): 31 – 34. (In Chinese)

[22] Li W C. Poison's mechanism and killing insects of sulfuryl fluoride. Chin J Frontier Health Quarantine, 2003, (2): 113 – 115. (In Chinese)

[23] Xu G G. Development of techniques and equipments for sulfuryl fluoride (SO2F2) fumigation. Plant quarantine, 1998, 12 (1): 38 – 46. (In Chinese)

[24] Chemical Reagent General Rules for the Gas Chromatography (GB/T9722 – 1988). Issued by the State Bureau of Technical Supervision, P. R. China, 5 September, 1988

[25] Maximum Levels of Contaminants in Foods (GB2762 – 2005). Issued National Department of Health of P. R. China and National Standards Committee of P. R. China, 25 January, 2005