0610

Sulfuryl Fluoride – Efficacy against *Tribolium castaneum* and *Ephestia kuehniella* and Residues of the Gas in Flour after Fumigations of Mills

D. Klementz[1 *], W. Rassmann[2] and Ch. Reichmuth[3]

Abstract: Sulfuryl Fluoride (SF) as Profume® together with a computer program (Fumiguide®) has been registered by Dow AgroSciences in many countries for disinfestations against stored product pest insects mainly in empty structures e. g. mills. Due to strongly reduced efficacy at lower temperatures, the SF application is recommended together with thoroughly warming up the structure above 20 ℃. Based on a mill fumigation with SF (average ct – product 1,200 g · h/m, 20 ℃, 60 h), the authors discuss the efficacy of the gas towards the eggs of the Red flour beetle (*Tribolium castaneum*) and Mediterranean flour moth (*Ephestia kuehniella*). No development of eggs of *Ephestia kuehniella* occurred in 80% of the samples and in 44% of the *Tribolium* samples. The average survival rate for the moths in samples with incomplete control was 8% compared to untreated samples. This rate amounted to about 12% for the *Tribolium* samples with survivors. In large flour mills often residual flour remains inside during a fumigation due to economic reasons. This flour is not object of the treatment but picks up residues depending on the diffusion of the gas through internal walls. Data are reported on the formation of fluoride residues in flour in three such bins: 10.4 mgF^-/kg, 5.7 mgF^-/kg, and 2.9 mgF^-/kg, respectively. The European maximum residue limit for fluoride in flour will be 2 mg/kg from September 2008. One of the biggest advantages using the Fumiguide® is the precise and specific adjustment of several fumigation parameters according to the individual conditions of the fumigation. That includes the species and life stages of the pests, the gas tightness of the object, the temperature, the exposure time and the direction and strength of the wind. The impact of various parameters on effective fumigations will be discussed based on efficacy data as well as the formation of residues.

Introduction

Sulfuryl fluoride (SF) was developed in the late 1950s as a structural fumigant, mainly for termite control (Steward 1956) [1]. It is applied to buildings, which are covered with gas proof sheets or otherwise sealed. The gas provides good penetration, requires a short fumigation period of approximately 24 h against adult insects. The egg stage of many insects appears to be up to 10 times more tolerant than adult insects. SF is considered a practical alternative to MB for many uses, particularly for quarantine fumigation applications and for use in empty food processing facilities (Reichmuth et al. 1997) [2]. It is toxic to post-embryonic stages of insects (Kenaga 1957) [3] but the eggs of many species are very tolerant especially at low temperatures, requiring concentrations of over 50 g/m and exposures of up to three days for complete kill (Williams and Sprenkel 1990) [4]. Eggs of *Ephestia kuehniella* at 25℃ required a ct – product of about 1000 g · h/m to prevent hatch and 800 g · h/m to prevent emergence (Bell and Savvidou 1999) [5]. SF is currently registered for use under the trade name Vikane®. It is used in some European countries to control a wide range of pests including: wood-destroying beetles, furniture and carpet beetles and clothes moths. Research is ongoing to evaluate the potential of this chemical for timber treatment for plant quarantine purposes. Efforts are underway to develop treatment schedules to fumigate timber being imported into the USA, Europe and Japan to control wood-destroying beetles or fungal pathogens (Chambers and Millard 1995; Kappenberg 1998) [6,7].

Materials and Methods

Fumigation

The fumigation parameters are presented in Table 1. Concentrations of SF and ct – products within the fumigated object were determined by the fumigating company.

Julius K hn – Institute, Federal Research Centre for Cultivated Plants Institute for Ecological Chemistry, Plant Analysis and Stored Product Protection, K nigin – Luise – Strasse 19, 14195 *Berlin, Germany*

1. *dagmar. klementz@ jki. bund. de*
2. *werner. rassmann@ jki. bund. de, christoph*
3. *reichmuth@ jki. bund. de*

Table 1. fumigation parameter of a mill fumigation in Germany

Fumigated object	Complete flour mill with silos, cleaning facilities and locations, stairwells and all storage halls
Location of fumigated object	Germany
Size of the fumigated object	60 000 m^3
Heating of the object	no
fumigant	Profume (99.8% sulfuryl fluoride)
Fumigated volume (e. g. silo basement, mill, cleaning facilities)	20 000 m^3
Fumigant dosage	1 200 $g \cdot h/m^3$
Total SF amount, incl. replacement gas	ca. 2 000 kg
Fumigation date	2005
Fumigation time	60 h

Climate Conditions in the Mill during Fumigation

The temperature during the fumigation was recorded with nine dataloggers (Figure 1). Each of them was placed in different sample bags.

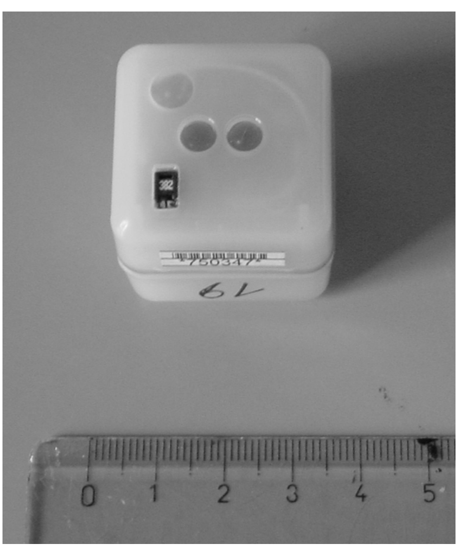

Fig. 1 Dataloggers for the detection of the temperature (mess scale in cm)

Determination of SF and Fluoride in non-fumigated Flour and Grain Silos

In large flour mills, often grain silos and bins for flour are constructed inside the whole building. For the miller, it is nearly impossible and totally unfeasible to empty these locations from the various products prior to fumigation. It would take more than a week after the fumigation to reproduce all these varieties of flour and refill the grain for the different customers. These parts of the mill are therefore not target of the treatment but pick up some gas due to diffusion of SF through walls. Since data were lacking on the possible formation of residues of SF and fluoride in flour, these in-house bins were supplied with measuring lines.

Adjacent to the fumigated area within the building, concentration of SF was automatically detected by use of a process gas chromatograph in three locations (results see Fig. 4). For this purpose, measuring lines were introduced 30 – 50 cm deep into flour. The detection of fluoride occurred electrochemically with ion-sensitive electrode. The average recovery rate for spiking samples between 1 mg/kg and 25 mg/kg, was between 91.8% and 101.2%. The quantitative detection limit was 0.5 mg fluoride/kg flour.

Three single samples of about 2 kg were taken from 30 cm underneath the flour surface with a heavy special sampling device from three bins for later determination of possible fluoride residues.

Test Insects: *Tribolium castaneum* and *Ephestia kuehniella*

Both the rust red flour beetle, *Tribolium castaneum*, and the Mediterranean flour moth, *Ephestia kuehniella*, were taken from a long lasting cultures of the Institute for Stored Product Protection of the Federal Biological Research Centre for Agriculture and Forestry (since 1.1.2008: Julius Kuehn-Institute, Federal Research Centre for Cultivated Plants, Institute for Ecological Chemistry, Plant Analysis and Stored Product Protection).

Tribolium castaneum was cultivated at a temperature of 25℃ and a relative humidity of 65% on a nutrient mixture with yeast and hole meal wheat flour and *E. kuehniella* at a temperature of 22℃ and the same relative humidity on a nutrient mixture of wheat and fine wheat flour. The adult beetles and moths were chosen by random selection and introduced into a vessel, which was kept in a climatized room for 1 to 4 days. Fifty samples of *T. castaneum* (50 beetles and a mixture of one to five days old eggs (more than 150 per sample)) were placed into little film boxes. The bottoms of the boxes and the caps contained pieces of very fine stainless steel gauze (100 m) (Fig. 2) to allow quick penetration of the gas and to avoid escape of freshly emerging larvae. 30 mL of fine, whole meal wheat flour served as substrate for the insects in the cages. Another set of 50 film boxes contained 50 eggs each of *E. kuehniella*. The eggs were one to four days old and the cages supplied with 30 mL wheat as substrate.

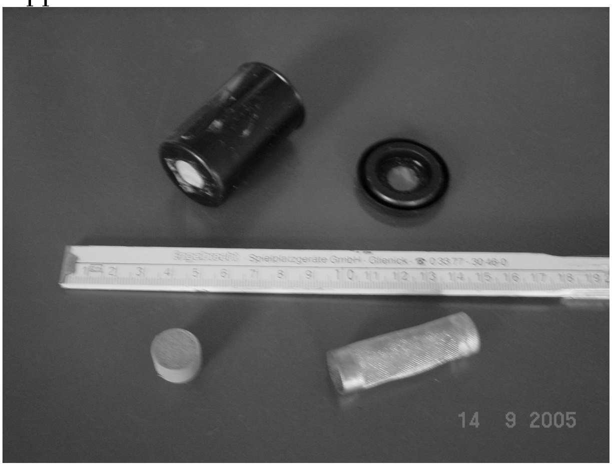

Fig. 2 Film boxes with stainless steel gauze

One sample at a time per species and stadium was packed in a cotton bag. All the bags were placed in different locations distributed over all floors of the mill.

One of two reference samples was taken to the mill the other remained in the laboratory under culture conditions. These samples were kept at similar climatic conditions without fumigation.

Following the fumigation, all samples were collected, transported back to the lab to 25℃ and 65% r · h. and bioassayed for twelve weeks for surviving or emerging insects.

Results

Temperature in the Mill during Fumigation

The temperature in the mill during fumigation presented in figure 3 was in the range 12 – 25℃.

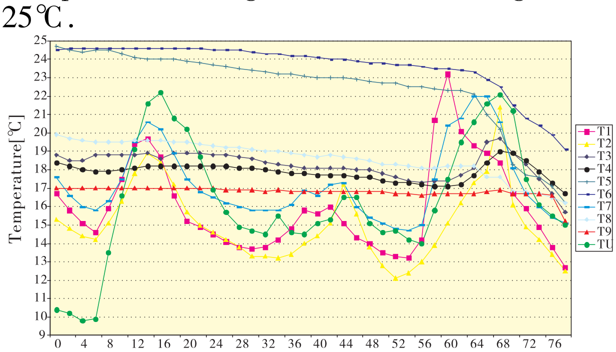

Fig. 3 Temperature on different places in the mill during fumigation with Sulfuryl fluoride

T1: 8. floor, cleaning location, on the window

T2: 3. floor, cleaning location, in one pipe

T3: 5. floor, cleaning location, on the window

T4: 3. floor, mill, in a sieve

T5: 2. floor, cleaning location, on the floor, near staircase

T6: 2. floor, mill, in one pipe

T7: 1. floor, mill, behind a metal cupboard

T8: 7. floor, storage silo, below a skylight

T9: cellar, elevator, E1

TU: behind the mill in a car

Detection of SF in Air in Flour Bins

Figure 4 describes the concentration characteristic of SF in various "untreated" silos in the fumigated mill. They picked up considerable amounts of the gas and were in so far unintentionally treated with low dosages of SF. The SF concentration 30 cm deep in the interstitial (between the particles of the flour) air in the flour within the "non-fumigated bins" reached about 60 to 80% of the values above the flour. The concentration in bin 32 and 26 were fairly similar, whereas only much less SF was detected in bin 23. The figure contains the average concentration in the flour as straight and dotted horizontal lines: bin 23: 1.2 gSF/m, bin 26: 4.6 gSF/m and bin 32: 4.2 g SF/m. After about 12 h and further on, additional gas was injected to compensate for losses to ensure sufficiently high ct – products. This addition is noticeable above and inside the flour. The concentrations in Figure 4 are increasing again after previous decay. In the course of the aeration after about 60 h some additional gas diffused into the cells.

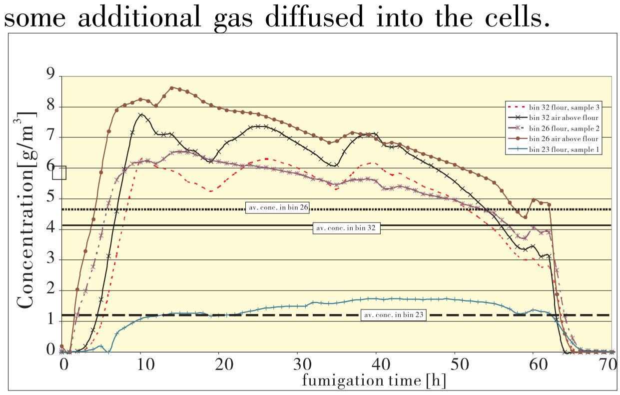

Fig. 4 Sulfuryl fluoride concentration in air during fumigation; 2 kg samples were taken for F^- residue analysis from underneath the surface (30 cm deep) in the bins 23 (sample 1), 26 (sample 2), 32 (sample3), respectively.

Detection of Fluoride in "Non – fumigated" Flour in Flour Bins

The average concentrations of SF as indicated in figure 4 and table 2 seemed to lead in tendency to higher or lower fluoride residues in the flour within the total exposure period of

60 h. The temperature was in the range of approximately 20℃. Figure 2 indicates temperatures during the treatment in various locations.

Table 2. Average SF concentration and fluoride amount in flour bins

Bin number	Sample number	SF concentration [g/m^3]	Fluoride amount [mg/kg]
32	3	4.22	5.7
26	2	4.59	10.4
23	1	1.17	2.9

Biological Efficacy

Out of 50 samples with *Ephestia kuehniella*, 4 moths on average emerged in 10 samples, so 20% of the samples had survivors. For the moths, the survival percentage was 8% compared to the untreated which was 100%. With *T. castaneum*, on average 31 beetles developed in 28 samples. That means that 56% of the samples were not fully controlled. The average value of 31 survivors corresponds to 12% of survivors in the untreated references with 263 emerging beetles as 100%.

Discussion

Obviously, also untreated concrete bins within fumigated flour mill buildings pick up a certain amount of gas. If 20 g/m is calculated as the average concentration in the fumigated area (1 200 g · h/m for 60 h), about 20% of this value was determined on top of the flour bins. The F^- – residues 30 cm deep in the flour amounted on average in all three investigated bins about 6 mg/kg. In 2005, Germany had fixed a provisional maximum residue limit (MRL) of 10 mg/kg. The European legislation asks for 2 mg/kg as MRL for grain from September 2008 onwards. Therefore, this subject has to be investigated in more detail to keep this type of fumigation of large flour mills with full in – house flour bins as an option. A better sealing of these bins with residual flour from the rest of the mill might be possible to reduce the formation of fluoride residues.

The lower limit for guaranteed efficacy predicted by the Fumiguide® program is 20℃. In the presented case, the temperature in some fumigated areas was below this value. To achieve complete mortality, these areas should have been warmed up. Also the indicated obtained ct-products on average 1200 g · h/m – were seemingly not sufficient for general complete control of all test insects. The miller had indicated that he was not interested in dosages for complete control where he had not found insects prior to the fumigation. The test samples were also placed into such areas. The concept of fumigating only the critical locations with high dosage within a building with connected areas and with low dosage in some others is very questionable. Gases tend to diffuse into all corners of a fumigated object within fairly short time. In so far, such a plan is futile.

In any case, only eggs as developing stages of the test insects survived to a certain degree (8% and 12% of untreated) in a limited number of samples (20% Ek and 56% Tc of the number of samples). Bell et al. (1999 and 2003) [8,9] as shown in table 3 reported as well that the eggs of *Tribolium* spp. are especially tolerant versus treatment with SF, especially at lower temperature than 30℃.

Table 3. ct – products for 100% reduction of emergence with sulfuryl fluoride fumigation (data from * Bell et al. [8] and ** Bell et al. [9])

Ct for 100% reduction of emergence (gh/m^3)			Species (most tolerant eggs)
15℃	25℃	30℃	
2016 *	764 *	–	*Ephestia kuehniella*
–	520 *	–	*Tribolium confusum*
–	1669 **	1154 *	*Tribolium castaneum*

In the presented fumigation, 1 200 g · h/m were not sufficient to obtain full control of all test insects at about 20 ℃ within 60 hours. SF has a very high potential to serve as suitable replacement gas for disinsectisation of empty premises like flour mills and other factories. If full control of all living stages of pest insects is the goal, ct – products and temperature must fit together. Also Reichmuth et al. [10] stressed this point. One of the biggest advantages using the Fumiguide® is the precise and specific adjustment of several fumigation parameters according to the individual conditions of the fumigation. That includes the species and life stages of the pests, the gas tightness of the object, the temperature, the exposure time and the direction and strength of the wind. The increase of temperature within an object can help to reduce the amount of gas.

References

[1] Steward, D., 1956. Sulfuryl fluoride a new fumigant for control the drywood termite, *Kalotermes minor* Hagen, Journal of Economic Entomology 50, 7

[2] Reichmuth, Ch.; Sch ller, M.; Dugast, J. – F.;

Drinkall, M. J. 1997: On the efficacy of sulfuryl fluoride against stored – product pest moths and beetles. *In*: Donahaye, E. J.; Navarro, S.; Varnava, A. *ed. Proc. Int. Conf. Contr. Atm. Fum. St. Prod.*, 1996, Printco Ltd., Nicosia, Cyprus. Pp. 17 – 23

[3] Kenaga, E. E. 1957: Some properties of sulphuryl fluoride as an insecticidal fumigant. *J. Econ. Ent.* 50: 1 – 6

[4] Williams, L. H.; Sprenkel, R. J. 1990: Ovicidal activity of sulfuryl fluoride to anobiid and lyctid beetle eggs of various ages. *J. Ent. Science* 25: 366 – 375

[5] Bell, C. H.; Savvidou, N. 1999: The toxicity of Vikane (sulfuryl fluoride) to age groups of eggs of the Mediterranean flour moth (Ephestia kuehniella). *J. St. Prod. Res.* 35: 233 – 247

[6] Chambers, D. M.; Millard, C. E. 1995: Assessing the global use potential of sulfuryl fluoride. *In*: *Proc. Ann. Int. Res. Conf. Methyl Bromide Alt. Em. Red.*, San Diego, California, USA. Pp. 83.1 – 83.2

[7] Kappenberg, K. W. 1998: Evaluierung alternativer Quarant netechniken zum Ersatz von Methylbromid bei der Behandlung nordamerikanischen Eichenholzes [Evaluation of alternative quarantine procedures for Northern American oak timber to replace MB]. *PhD thesis*, Albert-Ludwig-Universit t, Freiburg, Germany. 138 p

[8] Bell, Ch. H.; Savvidou, N.; Wontner Smith, T. J., 1999. The toxicity of sulfuryl fluoride (Vikane) to eggs of insect pests of lour mill. Proceedings of the 7th International Working Conference on Stored Product Protection, 14 – 19 October 1998 in Beijing, P. R. China, 345 – 350

[9] Bell Ch. H.; Wontner-Smith T. J.; Savvidou N., 2003. Some properties of sulphuryl fluoride in relation to its use as a fumigant in the cereals industry. Advances in stored product protection. Proceedings of the 8th International Working Conference on Stored Product Protection, York, UK, 22 – 26 July 2002, 910 – 915

[10] Reichmuth, Ch.; Rassmann, W.; Binker, G., Frba, G and Drinkall, M. J. 2003. Disinfestation of rust-red flour beetle (*Tribolium castaneum*), saw-toothed grain beetle (*Oryzaephilus surinamensis*), yellow meal worm (*Tenebrio molitor*), Mediterranean flour moth (*Ephestia kuehniella*) and Indian meal moth (*Plodia interpunctella*) with sulfuryl fluoride, advances in stored product protection. Proceedings of the 8th International Working Conference on Stored Product Protection, York, UK, 22 – 26 July 2002, 736 – 738