PS6-1-6173

Factors affecting the efficacy of sulphuryl fluoride as a fumigant

*C.H. Bell[1]**

Abstract

Sulphuryl fluoride, also known as sulfuryl difluoride, is being registered by Dow AgroSciences in a number of countries for use on food commodities and in food production facilities as the cylinder-based fumigant ProFume™. The fumigant is effective against all life stages of insects. Eggs compared to post-embryonic stages are more tolerant of the fumigant, and this needs to be taken into account for dosing strategies. Crucial factors for limiting egg tolerance are temperature and length of exposure, which operate differently on different species. For example concentration-time products (CTPs) of about 800, 600 and 300 g h/m^3 killed 95 % of eggs of *Rhyzopertha dominica* at 20, 25 and 30 ^{o}C respectively. At 30 ^{o}C, the CTP required for complete kill of eggs fell steadily from 300 g h/m^3 as the exposure time was lengthened from 20 h, only 155 g h m^{-3} being required over a 120 h exposure. For *Sitophilus granarius*, however, concentration rather than time was the more important component of the CTP at 25 ^{o}C, except below 15 g m^{-3} when exposure times longer than two or three days were encountered. A similar effect was seen for eggs of *Ephestia kuehniella*. A 'Fumiguide™ Program for ProFume™ gas fumigant' has been developed by Dow to deal with the complexities of the CTP relationship. The dosages prescribed in this computer-based program have been developed from research results and validated through successful commercial fumigations. Sulphuryl fluoride is stable up to 400 ^{o}C and can be used safely in conjunction with heating equipment. Electronic equipment including computers have been exposed to accumulative CTPs equivalent to over 30 commercial treatments at 50 ^{o}C+ without any observed detrimental effects. Results are also presented demonstrating that the gas is an excellent penetrant though layers of flour while being effectively contained by LDPE sheeting or oil-based paints.

Key words: fumigation; sealing; penetration; permeability; stored-product insects.

Introduction

ProFume™ has now been registered in several countries as a replacement of methyl bromide (MB) for treatment of empty structures, food processing facilities such as flour mills, and certain commodity groups, notably cereal grains, dried fruit and nuts. Further registrations in other countries and for different commodities are in progress. Tests on the active ingredient sulphuryl fluoride (SF) have been conducted on a wide range of stored product pests. Wide differences occur between the tolerance levels for different species and developmental stages. In all species, eggs proved the most tolerant life stage (Kenaga, 1957; 1961; Su and Scheffrahn, 1990; Williams and Sprenkel, 1990). The early discovery that eggs of many species were hard to kill gave rise to concerns over the practicality of choosing SF as a replacement for MB, an excellent insect ovicide. Nevertheless with appropriate dosing strategies it is possible to achieve satisfactory

[1] Central Science Laboratory, Sand Hutton, York YO41 1LZ, UK. Tel.: +44 1904 462104, fax: +44 1904 462111. E-mail address: c.bell@csl.gov.uk

control of eggs of even tolerant species such as *Tribolium castaneum* (Herbst) and *Ahasverus advena* (Waltl.). For stages other than eggs, the dosages of SF required for control are low, even at lower temperature (Kenaga, 1961; Su et al., 1989; Bell and Drinkall, 2000). Dow AgroSciences have developed a comprehensive software package, the Fumiguide, to enable rapid calculation of the dosage rates that need to be applied in a wide variety of situations and this approach has been validated by recent use in commercial practice.

Eggs of most stored product pests normally last only a few days at temperature in the upper half of the developmental range. It has been demonstrated that development of eggs does proceed, although possibly at a reduced rate, during exposure to SF (Bell et al., 2004). Hence time of exposure is an important factor in the toxicity of SF to eggs, which become highly susceptible to SF near the time of hatch.

With most fumigants, a particular concentration time product (CTP), derived from a gas concentration level in g m^{-3} multiplied by time of exposure in hours, gives a similar level of kill whether or not a higher or lower concentration (and corresponding shorter or longer exposure period) is employed. For some fumigants such as phosphine, however, time of exposure is more important than concentration in contributing to overall efficacy (Bell, 1979; 1992). For SF, like phosphine, extending the exposure period to span the tolerant egg phase could increase the efficacy of treatment for various commodities in store. Data have been acquired on the dosages of SF needed to kill eggs of different pest species with shorter (24-48 h) and longer exposure periods (2 to 7 days) and the results of some tests conducted on this aspect are presented here.

Besides the efficacy against target species, many other properties are important for the successful use of a fumigant gas. SF has many advantages as a replacement for MB; it is non-reactive with structural materials and components of electronic equipment, is non flammable and has not caused problems of taint following treatment of a wide range of materials (Kenaga, 1957). Published research indicates that SF is a very good penetrant of various materials (Kenaga, 1957, Stewart, 1957; Gray, 1960; Scheffrahn et al., 1992) and in this respect is more efficient than MB, which is a significant benefit in situations where insect infestations are located deep within cracks or machinery in premises such as flour mills. Here, if penetration is poor pockets of survival will occur and re-infestation of other areas will follow very rapidly, causing a fumigation failure.

On the other hand, it is essential that a fumigant gas can be adequately retained in a fumigation enclosure by appropriate sealing methods. Similarly, with much electronic equipment being present in modern food manufacturing premises, confidence is needed that repeated treatments with the fumigant will not cause any detrimental effects, a scenario that has restricted the use of the fumigant phosphine in such situations (Brigham, 1998).

In addition to studying the effects on insects, the experiments described here aimed to investigate the effect of SF on electronic equipment in the presence of heating equipment, to provide comparative data for SF and MB on the penetration rate and sorption in flour in relation to commercial treatments in flour mills, and for the permeability of SF and MB through various sealing materials.

Methods

Insect toxicity tests

Laboratory stocks reared at constant temperature and humidity provided insects for tests. Internal grain feeders such as *Rhyzopertha dominica* (F.) were reared on whole-wheat grain while other species were reared on the most suitable food media as established by laboratory rearing methods. Groups of several hundred adults of beetle species were set up to oviposit in a large crystallising dish containing either wheat grains for obligate internal grain feeders or for others, a thin layer of wholemeal flour sieved through a 10 mesh sieve to remove lumps. Dishes were incubated for three days at 25 °C, 70 % r.h.

To obtain eggs of moth species, freshly-emerged adults were collected by momentarily anaesthetising a culture with carbon dioxide and confining them in a plastic sieve with a glass dish. Drinking water was provided and the sieve was placed over a collecting dish in a holding room at 25 °C, 60-65 % r.h. in a 16 h light, 8 h dark lighting regime. Eggs were laid mostly in the first few hours of darkness of the first few cycles, and sufficient numbers for testing could usually be obtained from one such cycle (Bell, 1981).

Replicate samples of 25 g of grain or fifty 0-3 day-old eggs of each species were then carefully added to 100 ml count jars containing food medium, and placed at the fumigation temperature (see below) ready for fumigation. For tests on larvae or pupae, jars were incubated at the rearing temperature for the appropriate time before moving to the fumigation temperature the day before fumigation. Adults for testing were counted out in duplicate batches of 50 for each treatment on the day before fumigation.

The fumigation chambers used for the tests were of stainless steel construction ranging from 0.4 to 1.7 m^3 capacity, and were held in controlled temperature and humidity rooms. The chambers are fitted with ports and valves to allow for insertion of experimental material, the taking of gas samples through 2 mm bore nylon gas lines, and the evacuation of gas through the piping system connected to the building roof vents. After establishing the experimental temperature and before insertion of experimental material, fumigant gas was dosed from a commercial cylinder of SF into a partially evacuated chamber (to minimize risk of gas loss into the room). The desired gas concentration was obtained by checking concentration levels with a gas chromatograph fitted with a thermal conductivity detector and topping up or removing gas as necessary. On the day after establishing the required concentration, insect material was inserted into the chamber to commence fumigation.

The chamber was sampled for gas concentration after loading and before withdrawal of experimental material at the end of the allotted exposure. Samples were then left to air off in the fumigation room for up to a day before being returned to the rearing room for incubation at the rearing temperature. All jars containing immature stages were incubated until survivors emerged as adults. On the appearance of adults in control cultures, count jars and dishes were examined at least weekly and adults emerging were counted and removed until sufficient time had elapsed for all survivors to emerge.

Results from fumigation tests for each species and stage and at each temperature were analysed using probits by the method of Finney, correcting sample number for the number emerging as adults in the control and nil response treatments.

Effect of heat and SF on electronic equipment

Two computers, one switched on, were set up in a gas tight brick-built chamber which was then dosed repeatedly with varying amounts of SF. The computers were tested after each of eleven exposures by doing a few simple calculations using Microsoft Excel after each exposure. The last five exposures which together achieved a cumulative CTP of over 30,000 g h^{-1} m^{-3} featured the presence of a convectional air heater (ThermoNox GMBH, Germany) running at a 9 kW heat output in the chamber which raised the exposure temperature to between 50 and 70 °C for several hours at a time in each run. These units are in commercial use for heat treatment of mills in Europe and comprise two 9 kW heating elements across which a 750 W fan maintains a powerful air stream. Thermostat safety devices ensure that the elements shut down whenever the temperature of the incoming airflow exceeds a pre-set value. The heating elements thus provide a black heat source with maximum surface temperatures of around 200 °C.

Sorption study

A weighed quantity of fine wholemeal wheat flour, or feed wheat grain, was placed in a stainless steel chamber which was then dosed with SF at rates between 60 and 80 g m^{-3}. The loss of concentration due to sorption was monitored over 24 hours using a thermal conductivity meter. The tests were repeated with MB at a similar dosage rate for comparison with SF.

Penetration studies

A polyethylene bin was lined with an almost impermeable laminate film (Bromotec™) to prevent penetration of SF through the sides and then filled with fine wholemeal flour. Three gauze-capped 250 ml glass beakers were buried in the flour at depths of 10, 20 and 30 cm below the surface to act as air reservoirs for sampling. One end of a gas line was placed in each of the three beakers. The flour was packed into the bin as densely as possible by pressing down on the surface at various depths as the bin was filled. A fourth gas line was then placed on the surface. The bin was then placed in a chamber which was dosed with 20 g m^{-3} of SF. Concentrations were monitored using a gas chromatograph until SF concentrations reached 60 % of the surface concentration at 30 cm depth.

Replicate tests were performed at four different temperatures between 18 and 28 ^{o}C. A similar test was run for comparison using MB at 21 ^{o}C (Bell et al., 2003).

Permeability studies

Two types of plastic film, plywood and two types of paint were tested for their permeability to SF and MB at 20 ^{o}C. Permeabilities were measured using an adaptation of the ASTM standard test method for resistance of protective clothing materials to permeation by liquids and gases as described by Wontner-Smith and Chakrabarti (1994).

The plastic sheets tested were 50 mm low density polyethylene (LDPE) and the virtually impermeable Bromotec™ film (VIF) of the type currently stipulated for use in the EU with MB. The paints tested were Leyland® vinyl matt emulsion and Dulux® white gloss. Two coats of each paint were applied by brush to a piece of paper to produce a film that could be tested. A four-layer plywood (4-ply) was tested, the edge being painted with gloss paint to prevent results being affected by permeation of gas through the edge.

Results and discussion

Toxicity studies on insect pests

Results obtained for several species have indicated that temperature and length of exposure affect the performance of SF to a marked degree. For most species the control of eggs is much easier to achieve at 25 –30 ^{o}C than at lower temperatures, and lengthening the exposure from 24 hours to several days can reduce the dosage required by 50 % or more. Against eggs, this effect can be seen clearly, for example, in the results obtained for the unrelated species *Rhyzopertha dominica* (F.) (Coleoptera: Bostrichidae) and *Acanthoscelides obtectus* (Say) (Coleoptera: Bruchidae) (Table 1). Table 1 also shows that even for tolerant species such as *Ahasverus advena* (Coleoptera: Silvanidae) under cool temperature conditions, length of exposure is the key to reducing the dosage levels required for control to the practically feasible level of 1,500 g h m^{-3}. The effect is linked with the development time of eggs at the temperature concerned. Hence for *R. dominica* where eggs can take 11 days to hatch at 25 ^{o}C (Arbogast, 1991), increasing exposure times from 1 to 5 days has little effect until the temperature is raised to 30 ^{o}C, while for *A. advena* with eggs starting to hatch a week after oviposition at 20 ^{o}C (Jacob, 1996), increasing the exposure from 4 to 7 days greatly affects tolerance at this temperature.

Eggs vary in tolerance to SF during their development and this presents another source of

Table 1. Sulphuryl fluoride: Examples of CTPs (g.h m^{-3}) required for kill of eggs of three storage beetles, *Rhyzopertha dominica* (*R.d.*), *Ahasverus advena* (*A.a.*) and *Acanthoscelides obtectus* (*A.o.*), at various temperatures and exposure periods.

Species	Temp.	Exposure	Maximum CTP survived		LD_{50} / LD_{95} from	Lowest CTP needed for
	(°C)	(h)	g h m^{-3}	% survival	Probit line	100 % control
R. d.	20	20	792	3.8	320/706	912
		58	574	11.8	251/816	762
		120	672	11.4	373/761	939
	25	20	422	8.9	203/498	656
		58	423	7.1	194/457	525
		120	594	1.4[1]	143/613	638
	30	20	294	2.9	156/405	415
		58	242	12.9	80/593	304
		120	124	6.5	<50/-	155
A.a.	20	40[2]	3,824	3.8	1,685/3761	4,656
		96	2,323	18.4	1,052/3707	3,072
		168	1,520	3.2	784/1421	1,966
A.o.	20	24	727	1.2[1]	215/541	1,070
		96	456	8.9	173/579	605
	25	24	554	3.2	242/690	763
		48	290	1.5[1]	126/244	379
	30	24	413	10.5	105/337	480
		48	159	2.3	79/130	259

[1] Represents a single survivor at these dosages.

[2] Maximum exposure length at LD95 from tests at fixed concentration levels

deviation from the rule that a particular CTP can be expected to achieve the same level of control regardless of concentration level and exposure period. When operating with shorter exposure times, the general trend that lengthening exposure time will reduce the dosage required for control may be reversed as seen in Figure 1 for concentrations above 15 g m^{-3} at 25 °C for Mediterranean flour moth *Ephestia kuehniella* Zeller and granary weevil *Sitophilus granarius* (L.). In each case there was a temperature-dependent point beyond which extending exposure time became beneficial rather than detrimental towards achieving control. In summary, besides the benefit of increased temperature, efficacy will always be improved if exposure time can be lengthened sufficiently.

Effect of heat and SF on electronic equipment

The computers showed no sign of ill effect after any of the exposures, even after exposures with temperatures reaching 65 to 70 °C, and withstood an accrued CTP of over 42,000 g h m^{-3}, a dosage equivalent to about 30 practical mill fumigations. It can therefore be concluded that regular use of SF fumigation at elevated temperatures as a control strategy should not cause problems to arise with electronic equipment in flour mills or food processing facilities.

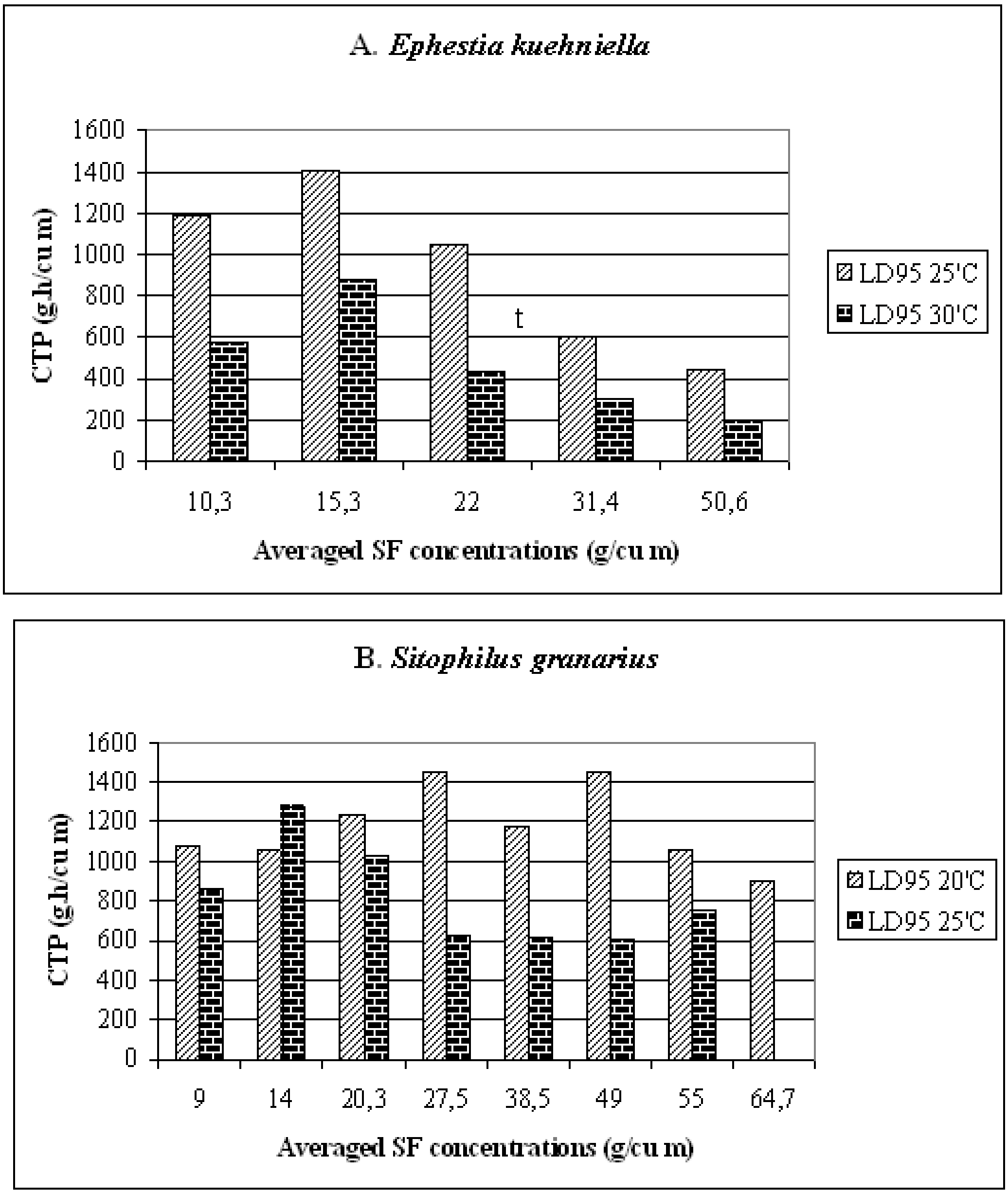

Figure 1. The effect of concentration level on the Concentration-Time Product (CTP) required for 95 % kill of two grain pests, A. the Mediterranean flour moth *Ephestia kueniella* and B. the granary weevil *Sitophilus granarius.*

Sorption and penetration studies

There was at least a ten-fold difference in the levels of fumigant sorbed by flour at 25 °C between MB and SF. The sorption of MB on flour was 750 mg/kg while the sorption of SF was less than 75 mg/kg, i.e. too low to be measured by the method of detecting a lowering of gas concentration in the chamber. SF was also found to penetrate flour about 10 times faster than MB, concentrations at a depth of 30 cm reaching 60 % of the surface level within 3 hours at 21 °C (Bell et al., 2003). No significant effect of temperature on penetration time was observed between test runs at 18 – 28 °C (Bell et al., 2004).

Other studies have shown that SF is a good penetrant. The gas diffused through a 28 cm column of sawdust without difficulty (Stewart, 1957), through 9 inches (23 cm) depths of flour, ground tobacco and dried milk powder (Kenaga, 1957), and through 2 inch (5 cm) thick Douglas fir blocks (Gray, 1960), killing pests enclosed. In studies based on gas measurements rather than bioassays, SF was shown to penetrate pine wood disks of 2.5 cm thickness within 20 hours, though diffusion through hard wood was much slower, and was further restricted if the wood was painted or hydrated by soaking (Scheffrahn et al., 1992). Apart from the case of soaked hard wood, SF has always proved better at penetrating commodities than MB.

Permeability studies

Permeability was much lower for SF than for MB in all cases except for the emulsion paint and the plywood, which provided no barrier against gas loss (Table 2). The gloss paint and VIF sheeting provided a much better barrier to both gases. The 50 mm LDPE provided a highly effective barrier to SF (even better than for phosphine) and the use of the more expensive VIF sheeting would thus not be necessary for this gas under normal circumstances. However, there are circumstances during the treatment of food processing facilities where the exposure of sorptive food products on the premises cannot be allowed, and here careful sealing of areas containing such products from the fumigation area using an approved VIF sheeting would provide an effective solution.

References

Arbogast, R. T., 1991. Beetles: Coleoptera. In: Gorham, J. R. (Ed.), Ecology and Management of Food-Industry Pests, AOAC, Arlington, VA USA, pp.131-176.

Bell, C. H., 1979. The efficiency of phosphine against diapausing larvae of *Ephestia elutella* (Lepidoptera) over a wide range of concentrations and exposure times. Journal of Stored Products Research 15, 53-58.

Bell, C. H., 1981. The influence of light cycle and circadian rhythm on oviposition in five pyralid moth pests of stored products. Physiological Entomology 6, 231-239.

Bell, C. H., 1992. Time, concentration and temperature relationships for phosphine toxicity in tests on diapausing larvae of *Ephestia elutella* (Hubner) Lepidoptera: Pyralidae). Pesticide Science 35, 255-264.

Bell, C. H., Drinkall, M. J., 2000. Sulfuryl fluoride to replace methyl bromide use in the flour milling industry. Annual International Conference on Methyl Bromide Alternatives and Emissions Reductions, MBAO, Orlando, Florida, November 2000, Paper 75, 3pp.

Table 2. The permeability of various sheeting materials to sulphuryl fluoride and methyl bromide.

Material under test	Permeability to sulphuryl fluoride (g h^{-1} m^{-2})	Permeability to methyl bromide (g h^{-1} m^{-2})
50 ì m LDPE	0.21[1]	50
VIF	0	0.15
Gloss Paint	0.01	14.4
Emulsion Paint	No barrier	No barrier
Plywood	No barrier	No barrier

[1] An equivalent result for phosphine would be 1.5 g h^{-1} m^{-2}

Bell, C.H., Savvidou, N., Wontner-smith, T.J., Cardwell, S.K., Bodle, C., 2004. Development of sulphuryl fluoride as a fumigant for the milling industry. HGCA Project Report No. 333, Home-Grown Cereals Authority, London, 67pp.

Bell, C.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. In: CRedland, P.F., Armitage, D.M., Bell, C.H., Cogan, P.M., Highley, E. (Eds), Advances in Stored Product Protection, Proceedings of the 8th International Working Conference on Stored Product Protection, York, UK, July 22-26 2002, CAB International, pp.910-915.

Brigham, R.J., 1998. Corrosive effects of phosphine, carbon dioxide, heat and humidity on electronic equipment. Canada/ US Methyl Bromide Working Group Report.

Gray, H.E., 1960. Vikane, a new fumigant for control of drywood termites. Pest Control 28, 43-46.

Jacob, T.A., 1996. The effect of constant temperature and humidity on the development, longevity and productivity of *Ahasverus advena* (Waltl.) (Coleoptera: Silvanidae). Journal of Stored Products Research 32, 115-121.

Kenaga, E.E., 1957. Some biological, chemical and physical properties of sulfuryl fluoride as an insecticidal fumigant. Journal of Economic Entomology 50, 1-6.

Kenaga, E.E., 1961. Time, temperature and dosage relationships of several insecticidal fumigants. Journal of Economic Entomology 54, 337-342.

Scheffrahn, R.H., Su, N.-Y., Hsu, R.C., 1992. Diffusion of methyl bromide and sulfuryl fluoride through selected structural wood matrices during fumigation. Material und Organismen 27, 147-155.

Stewart, D., 1957. Sulfuryl fluoride - a new fumigant for the control of the drywood termite *Kalotermes minor* Hagen. Journal of Economic Entomology 50, 7-11.

Su, N.-Y., Osbrink, W.L.A., Scheffrahn, R.H., 1989. Concentration-time relationship for fumigant efficacy of sulfuryl fluoride against the Formosan subterranean termite (Isoptera, Rhinotermitidae). Journal of Economic Entomology 82, 156-158.

Su, N.-Y., Scheffrahn, R.H., 1990. Efficacy of sulfuryl fluoride against four beetle pests of museums (Coleoptera: Dermestidae, Anobiidae). Journal of Economic Entomology 83, 879-882.

Williams, L.H., Sprenkel, R.J., 1990. Ovicidal activity of sulfuryl fluoride to anobiid and lyctid beetle eggs of various ages. Journal of Entomological Science 25, 366-375.

Wontner-Smith, T.J., Chakrabarti, B., 1994. Measurement of permeability of plastic sheeting to fumigant gases. International Pest Control 36, 15-17.