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Application Researches on Fumigation by Combination Sulfuryl Fluoride with Carbon Dioxide in Cereals

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Abstract: Based upon that median lethal dose(LD_{50}) of such beetles against Sulfuryl Fluoride (SF) as *Sitophilus zeamais*, *Oryzaephilus surinamensis*, *Rhizopertha dominica*, *Cryptolestes ferrugineus* and so on have been tested, while fumigation for 14 – 16 days by combination SF , which at different concentration such as 3g/m^3, 5g/m^3, 10g/m^3 and so on, with Carbon Dioxide at the concentration of 100g/m^3, egg, larva and pupa of *Sitophilus zeamais* in wheat and maize bulks could be killed completely. Through fumigation by combination SF with Carbon Dioxide in grain stored granaries, it showed that the residual of SF left lower after fumigation, and meanwhile it also could control effectively adults, eggs, larva and pupa of some main grain storage pests, such as *Tribolium castaneum* (with phosphine resistance or sensitivity), *Rhizopertha dominica* (with phosphine resistance or sensitivity), *Sitophilus zeamais* and so on.

Key words: Sulfuryl Fluoride, cereals, fumigation, grain storage pests

Preface

As early as 1901, Sulfuryl Fluoride (SF) has been produced in laboratory by H. Morssan in France. In 1957, it has been developed as commodity by Dow Elan Co. in America, which named as Vikane. In China, it was Mr. Xu GuoGan who raised to develop SF in 1975, and in 1978, it has been classified as emphasis research project by Ministry of Agriculture. Presided, leaded to organize and cooperate by Mr Xu, it was developed into product in 1983.

As one of Nerve Agents Poisoning, SF has excellent activities against insects, murine, Amphioxus, plants trichite and so on, which has been used for many industries, such as healthy quarantine, plant quarantine, commidity maintenance, products of a culture protection, pests control in ancient building and herbarium museum and so on. Since its excellent physicochemical properties, including difficult to burn, no influence on the ozone layer, large vapor tension, strong penetration capability, easy to diffuse and so on, it has been gotten application and promotion as fumigants. Besides of these, it also was safe to metal instruments, nature fiber or textile products, paper, leather and others chemical fibra. For middle toxicity, which there was no carcinogenic, teratogenic and mutagenic problems by animal testing, it could be applied in safety.

Rudimental researches on application with SF to control grain storage pests and wood insects have been carried on before 1983 by Mr Xu et al, and in 1989, it was used for controlling grain storage pests in crops seeds granary of of Crop Germplasm resources, Chinese Academy of Agricultural Sciences. Since 2004, application researches on SF to control grain storage pests have been carried on systemicly by Mr Xu and LongKou Chemical Plants.

In America, SF has been allowed to registrate for controlling storage pests in grain and their products storage, or in 14 kinds of dry fruits and nuts storage. In December 2005, World Healthy Organization (WHO) and Food and Agriculture Organization of the United Nations (FAO) held the international conference on developing the standards of pesticide residual. There were several biochemistry properties of SF which have been pointed out in this international conference. The first one was the direction of SF in people and animals bodies. While automatic tracer of ^{35}S tagged SF at the concentration of 30μL/L and 300μL/L (that was 0. 1365g/m^3 and 1. 36g/m^3), the tracer would be ingested quickly. It took 4 hours to get the terminal maximum concentration in blood plasma and akaryocyte. By determination the content of fluorosulfuric acid and sulfuric acid, it showed that SF would hydrolyze into fluorosulfuric acid and fluoride, and went on hydrolization into sulfuric

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acid and fluoride further. As the content of fluoride in rats' blood and urine increasing after fumigation SF, it also showed that SF would be decomposed and excreted. As fluorosulfuric acid residual was produced by SF hydrolyzation, it would means nothing than the nature producing. It was addressed in the international conference that residual was the total amount of fluorion in cereals. After fumigation with SF in wheat, maize, paddy, barley, oats bulks, the maximum residual concentration of SF was 0.05mg/kg, and the hazard residual (HR) was 0.08mg/kg. The fluorion hazard residual in cereals was 21mg/kg, Supervised Trial Medium Residue (STMR) in cereal was 3.5mg/kg.

Testing Indoors

Experimental Materials

SF Fumigants, produced in LongKou city Chemical Plant. barley

Experimental Methods

Experimental container

The volume of glass bottle was determinated by weighing method with water. Gubber bung should be fit suitably in glass bottle mouth and its bottom debouch and jam – pack, a piece of glass tube was plugged tightly into the middle of rubber bung in glass bottle mouth, its inferior extremity located in the place of grain surface, the superior extremity exposed out of bottle mouth and coated into latex tubing. As the same method as glass bottle mouth, a piece of glass tube was plugged tightly into the middle of rubber bung in bottom debouch, which strenching into the center of glass bottle, and there were few pore in its extremity, the copper tube, which out of bottle, should be coated latex tubing tightly. The hose in glass bottle mouth was used for application and air exhausting to analyze the concentration of SF and Carbon Dioxide in the upper part, the copper tube in bottom debouch was used for determination the concentration of SF and Carbon Dioxide in the bottom.

Inspection methods

The concentration of SF and Carbon Dioxide matched, the residual concentration would be inspected by conductance system in gas chromatogram and electron capture system.

Grain species

According to the situation of grain storage, wheat or maize in the bottle filled about 60% of its capacity, including wheat 14 kilogram weight, maize 12 kilogram weight.

Pests sample and their placing

Sitophilus zeamais tested which purified for 2 generations, adults after hatching for 16 days, eggs and larvae which produced in maize or wheat for 6, 8 and 14 days, mixture pests which consisted of adults, eggs, larvae and pupa.

Sweetmeats insects (adult, larva, pupa), *Tribolium castaneum* (adult, larva), *Rhizopertha dominica* (adult), longhorned flour beetle (adult), *Cryptolestes ferrugineus* (adult).

All of adults, larvae and pupa should be put into glass tube with feeds together, and sealed with nylon cloth and adhesive tapes at both extremities. To wheat or maize or rice with *Sitophilus zeamais* eggs, larvae and pupa, they should be stored in micro-nylon bags, which mouth should be tightened with strings. While pest samples tested lying in the bottom of glass bottle, it should be filled up with such filling-materials as wheat or maize.

Method on determination temperature

While thermometer was plugged into filling-materials, temperature should be made record at 8:00 a. m, 13:30 p. m, 16:30 p. m everyday. At end of experiment, the maximum temperature, the minimum temperature and accumulated temperature should be recorded in experimental period.

Calculation on dosage

Both of SF and Carbon Dioxide calculated their weight by volume of mole vapor, and the necessary volume applied by the volume of bottle and glass syringe of 100mL. At 25℃, these gas densities of SF and Carbon Dioxide was 0.0045mg/mL and 0.0018mg/mL respectively.

Chemicals application

When pressure regulator and sebific ducts contacted with the mouth of SF cylinder gradually, spigot should be opened slowly. After modulating the pressure regulator, plugged the glass syringe into the sebific ducts for collecting the necessary Sulfuryl Flulride, and then poured them into the bottle. The method for collecting 100mL of Carbon Dioxide was as the same as collecting SF. When collecting carbon dioxide, please exhaust and inlet gas again and again for well-distribution. At last, the total gas consumption would be made up with collecting carbon dioxide.

Effect inspection

After taking pests tested out from experimental bottle and gas exhausting for several hours, pests should put into constant temperature and humidity chamber for culture (temperature at 28℃, humidity at about 60%). The first check should be begun when adults pests were observed at emergence in control group. For re-

ducing interference, adults should be killed and checked out every time. There would be checked for several times and the last should remain 53 days, 54 days, 71 days before the end of experiment.

Results

determination results of median lethal dose which grain storage pests adults against SF

When fumigatiom with SF alone for 16hours in empty bottle at 15 – 10℃, median lethal dose (LD_{50}) of *Sitophilus zeamais*, sawed flour beetle, *Rhizopertha dominica*, *Cryptolestes ferrugineus*, longhorned flour beetle, Sweetmeats insects and *Tribolium castaneum* equals to 2.512g/m^3, 1.4125g/m^3, 1.972g/m^3, 1.274 g/m^3, 1.274g/m^3, 3.715g/m^3, 7.446g/m^3 respectively.

Determination effect when the lethal ratios against *Sitophilus zeamais*, Sweetmeats insects, *Tribolium castaneum* were 100% by fumigation by combination SF with Carbon Dioxide.

When experiment was taken in 20L of glass bottles and filled with 60% of grain, the results were as follows(Table 1):

Table 1. Pests control effects while fumigation by combination SF with Carbon Dioxide

concentration		Exposure time(h)	Temperature (℃)	CT value(gh/m^3)		effects(at different CT value)		
SO_2F_2 (g/m^3)	CO_2 (g/m^3)			SO_2F_2	CO_2	*Sitophilus zeamais*	Sweetmeats insects	*Tribolium castaneum*
14.32g/m^3	12.40g/m^3	6	20	85.94	74.39	79.00%	40.62%	/
15.38g/m^3	73.58g/m^3	6	18 – 19	92.29	441.48	100%	96.78%	86.00%
14.59g/m^3	12.33g/m^3	8	19 – 20	116.70	98.64	100%	100%	96.77%
15.24g/m^3	33.21g/m^3	8	20	121.95	265.69	100%	100%	100%
17.79g/m^3	17.79g/m^3	8	19 – 20	142.32	184.16	100%	100%	100%

According to CT value of SF, it showed that the CT value of *Sitophilus zeamais*, Sweetmeats insects, *Tribolium castaneum* increased gradually.

Here were data of effect while fumigation for 14 days and 16 days against *Sitophilus zeamais* eggs, larvae and pupa by combination SF at different concentration (3g/m^3, 5g/m^3 and 10g/m^3) with Carbon Dioxide at high concentration. (Table 2)

Table 2. Effect while fumigation by combination SF with Carbon Dioxide against *Sitophilus zeamais* eggs, larvae and pupa

concentration		Filling – materials	temper -ature ℃	Expo -sure time (h)	CT value(gh/m^3)		The amount of adults		The amount of adults	
SO_2F_2 (g/m^3)	CO_2 (g/m^3)				SO_2 F2	CO_2	Weight of wheat (g)	amount	Weight of rice (g)	amount
10	108.0	wheat maize	11.0 ~ 15.5	16	3 840	41 472	215	0	/	/
5	116.0	wheat	12.0 ~ 19.0	14	1680	38976	115	0	133 133	0
3	115.0	wheat maize	11.0 ~ 15.0	16	1152	44160	202	0		0
3	120.9	wheat	12.0 ~ 18.0	14	1008	40622	115	0	133	0
0	148.5	wheat	11.5 ~ 18.0	16	/	57024	135	9	133	107
0	170.5	wheat maize	12.0 ~ 13.5	14	/	57288	176	220	/	/
0	0	wheat	12.0 – 19.0	14	/	/	115	20	133	150
0	0	wheat maize	11.5 ~ 13.0	16	/	/	163	251	/	/

From experimental results in Table 2, *Sitophilus zeamais* eggs, larvae and pupa could be

killed completely at low temperature while fumigation for 14 – 16 days by combination SF at different concentration (3g/m^3, 5g/m^3 and 10g/m^3) with Carbon Dioxide at 100g/m^3 of concentration. However, there were no effects while fumigation with 148. 5 – 170. 5g/m^3 of Carbon Dioxide for 14 – 16 days alone.

Here were controlling effects against *Sitophilus zeamais* eggs, larvae and pupa while fumigation with SF at 5g/m^3, 10g/m^3 alone, or with 30g/m^3 of Carbon Dioxide for 7 days or 10 days.

Table 3. Effect against *Sitophilus zeamais* eggs, larvae and pupa while fumigation with SF alone or by combination SF with Carbon Dioxide

concentration		Filling – materials	temper -ature (℃)	Expo -sure time (h)	CT value (gh/m^3)		Amount of adults	
SO_2F_2 (g/m^3)	CO_2 (g/m^3)				SO_2 F2	CO_2	Average amount of feeds (g)	amount
10	0	maize	13 – 14	7	1680	0	105.4	1
10	30	maize	13 – 14	7	1680	7200	101.5	0
5	0	maize	13 – 14	7	840	0	126.1	4
5	30	maize	13 – 14	7	840	5040	101.5	0
10	0	maize	13 – 14	10	2400	0	107.5	0
10	30	maize	13 – 14	10	2400	7200	114.8	0
0	0	maize	13 – 14	10	0	0	108.2	223.5

From the Table 3, many results could be concluded, such as (1) one *Sitophilus zeamais* adult has been observed at emergence after culture for 53 days while fumigation with 10g/m^3 of SF for 7 days without carbon dioxide, however, no adults appeared with 30g/m^3 of Carbon Dioxide furthermore. (2) four *Sitophilus zeamais* adults have been observed at emergence after culture for 53 days while fumigation with 5g/m^3 of SF for 7 days without carbon dioxide, however, no adults appeared with 30g/m^3 of Carbon Dioxide furthermore after 53 days. (3) if fumigation with 10g/m^3 of SF postponed exporsure time for 10 days, there would be no adults appearance after 53 days whether adding Carbon Dioxide or not. Therefore, carbon dioxide addition had synergistic action, but there also were redeeming and ensuring effects by postponing exposure time.

Influence on germination ratios of wheat and maize while fumigation by combination SF with Carbon Dioxide

Here (Table 4) were determination effects of influence on wheat or maize germination ratios while fumigation by combination SF at 5g/m^3, 10g/m^3 with 30g/m^3 of Carbon Dioxide for 15 days and 90 days, and while fumigation by combination SF at 5g/m^3 with 30g/m^3 of Carbon Dioxide for 30 days.

Table 4. Influence on germination ratios of wheat and maize while fumigation by combination SF with Carbon Dioxide

concentration		Exposure time (d)	CT value (gh/m^3)		Grain species tested	Germination ratios (%)	influence or not
SO_2F_2 (g/m^3)	CO_2 (g/m^3)		SO_2F_2	CO_2			
10g/m^3	30g/m^3	15	3600	10800	wheat	98.5	No
5g/m^3	30g/m^3	30	3600	21600	wheat	99.0	No
10g/m^3	30g/m^3	90	21600	64800	wheat	99.5	No
Control group		90			wheat	96.5	
10g/m^3	30g/m^3	15	3600	10800	maize	97.0	No
5g/m^3	30g/m^3	30	3600	21600	maize	94.5	No
10g/m^3	30g/m^3	90	21600	64800	maize	90.0	A little
Control group		90			maize	96.0	

From the table 4, there were no influence on wheat germination ratios while fumigation by

combination SF with 30g/m^3 of Carbon Dioxide, however, there were a little influence on maize while fumigation by combination SF at 10g/m^3 with Carbon Dioxide at 30g/m^3 for 90 days. Certainly, further experiment should be taken next time.

Discussion

Qualities of products: as there were such by-products as sulfonyl fluoride chlorine in process flow, some high-purity SF should be taken.

technical parameter: there were reference indexes while fumigation by combination SF with Carbon Dioxide at common temperature: fumigation by combination SF at 6g/m^3 with Carbon Dioxide at 10g/m^3 for 20 – 30 days, fumigation by combination SF at 8g/m^3 with Carbon Dioxide at 10g/m^3 for 15 days, fumigation by combination SF at 10g/m^3 with Carbon Dioxide at 10g/m^3 for 10 days. If taking fumigation with SF alone, pests also would be controlled. However, Carbon Dioxide addition could be favor of penetration abilities to assure pests control effects, and it would decrease the cereals absorption to SF.

Influence on grain seeds: as fumigation with SF at low dosage for long time could not only control grain storage pests effectively, but also there were no influence on germination ratios, the influence on grain seeds while fumigation with SF would be made researches further. Beside of some factors, such as purity of SF, dosage, fumigation time, diffusion or not, there were others including fresh degree of seeds, moisture content and reserving qualities which could make influence on seeds germination ratios.

Roles which Carbon Dioxide played in the fumigation: SF could penetrate under 6 meters in grain bulks whether mixing Carbon Dioxide or not. Cereals absorption to SF could be decreased by combination with Carbon Dioxide. It also was favor to SF well-distribution and promote penetration abilities by increasing pressure. In addition, it had synergistic effect on control pests by 10 g/m^3 of Carbon Dioxide addition.

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