Research on carbonyl sulfide as a fumigant for control of stored grain insects

Tan Xianchang, Hou Xingwei, Cheng Lizheng and Wu Jianchun

Abstract

Laboratory data showed that carbonyl sulfide (COS) was toxic to stored grain insects. After 24-h exposure time, the dosages for 100% control of adults were 7.28 mg/L to Rhizopertha dominica (F) and psocids, 14.5 mg/L to Oryzaephilus surinamensis (L.) and Callosobruchus chinensis (L.), 29.2 mg/L to Sitophilus oryzae (L.), Sitophilus zeamais (Motschulsky), Lasioderma serricorne (F.), Cryptolestes pusillus (Schonherr), Callosobruchus maculatus (F.), Trogoderma variabile (Ballion) and Tribolium castaneum (Herbst), 44.2 mg/L to Tribolium confusum (Jacquelin du Val). The most tolerant stages of T castaneum and T. confusum were the eggs and pupa.

COS reduced germination of maize, soybean, mung bean, wheat and paddy. The order of damage was maize > soybean > paddy > mung bean > wheat > sorghum > barley. COS might also cause changes in soybean color.

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COS had adverse effect on quality of wheat. Both the bread made from wheat fumigated with COS at the dosage above 50 mg/L and the rice made from paddy fumigated at the dosage above 100 mg/L after 6 months aeration, had an off odor.

COS at 12 - 29% could cause ignition or explosion by spark Ignition could be inhibited by adding CO2 half of the COS volume.

COS in the intergranular air space decayed quickly, and could keep 3 - 9 days during fumigation of grain. During aeration, there was an obvious smell of H2S in the grain fumigated with higher concentrations of COS, but no COS residue could be detected after 1 day aeration.

Field trails results showed that wheat and paddy fumigated with COS at a dosage of 50 g/m3 and 7 days exposure time controlled the pests in the grain.

Introduction

In China, stored grain is subject to infestation by more than 200 species of stored grain insect pests. Aluminum phosphate is the major compound for disinfestation of stored grain. More than 95% of stored grain in state warehouses was fumigated with phosphate each year. Owing to the appearance of resistance of stored grain insect pests to phosphate in China (Zeng L 1998), there is an urgent need for alternatives of phosphate fumigation of stored grain.

Carbonyl sulfide is similar to carbon disulfide and carbon dioxide, having properties between these two compounds. It is a kind of colorless, odorless and tasteless gas, but when the industrial products of carbonyl sulfide or pure COS is exposed in the air, a slight odor of hydrogen sulfide will be given off. Desmarchelier (1994) reported that carbonyl sulfide may replace methyl bromide and phosphine for fumigation. It is toxic to many of the major stored product insect pests. In the intergranular air space, carbonyl sulfide decays more slowly than methyl bromide. It has no adverse effect on the germination of wheat. Zettler et al. (1997) reported the toxicity of carbonyl sulfide to 5 species of stored product insects and considered it has the potential use as a fumigant of dried fruits and nuts.

This paper summarized the main results of laboratory experiments and field trials of carbonyl sulfide, which were carried out in China for control of stored, grain insect pests.

The Toxicity of Carbonyl Sulfide to Stored Grain Insect Pests

Test insects have been reared in laboratory on standard diets at 28°C and 70% r.h for several years. The test insects were Rhizopertha dominica (F.), Oryzaephilus surinamensis (L.), Callosobruchus chinensis (L.), Sitophilus oryzae (L.), Sitophilus zeamais (Motschulsky), Lasioderma serricorne (F.), Cryptolestes pusillus (Schonherr), Callosobruchus maculatus (F.), Trogoderma variabile (Ballion), Tribolium castaneum (Herbst), Tribolium confusum (Jacquelin du Val) and Psocid (a species of Liposceliidae).

Zhuzhou Pesticide Factory, Hunan Province provided industrial product of carbonyl sulfide. Its purity was higher than 99%, and it was stored in a steel canister for storage of liquefied petroleum gas.

Bioassays were conducted in 500 ml fumigation bottles with ground glass valve, a rubber tube was fitted between
the valve and a vacuum pump. Required concentrations of carbonyl sulfide were introduced by reducing pressure, and the system was equilibrated to atmosphere pressure after carbonyl sulfide was introduced. As assays were performed in triplicate, with 30 or 50 insects at 28°C. After 24-hours exposure time, apart from specially mentioned ones, insects were put in wheat for 7 days, then mortality was assessed and adjusted according to Abbott’s formula. Results were discarded when control mortality exceeded 10%.

### Table 1. Toxicity of carbonyl sulfide to major insects of stored grain.

<table>
<thead>
<tr>
<th>Insects</th>
<th>Mortality (%)</th>
<th>Concentration of carbonyl sulfide (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.45</td>
<td>2.91</td>
</tr>
<tr>
<td></td>
<td>7.28</td>
<td>14.5</td>
</tr>
<tr>
<td></td>
<td>29.2</td>
<td>43.7</td>
</tr>
<tr>
<td></td>
<td>72.8</td>
<td></td>
</tr>
<tr>
<td><em>R. dominica</em> (adults)²</td>
<td>94.6(4.1)</td>
<td>98.6(2.3)</td>
</tr>
<tr>
<td>Psocid</td>
<td>0</td>
<td>80.5(5.6)</td>
</tr>
<tr>
<td><em>O. surinamensis</em> (adults)</td>
<td>0.7</td>
<td>1.3</td>
</tr>
<tr>
<td><em>C. chinensis</em> (adults)²</td>
<td>1.3</td>
<td>0</td>
</tr>
<tr>
<td><em>S. oryzae</em> (adults)</td>
<td>12.6(1.5)</td>
<td>9.6(0.6)</td>
</tr>
<tr>
<td><em>S. zeamais</em> (adults)</td>
<td>1.3</td>
<td>1.6(0.6)</td>
</tr>
<tr>
<td><em>L. serricorne</em> (adults)²</td>
<td>7.8(5.0)</td>
<td>27.1(3.5)</td>
</tr>
<tr>
<td><em>C. pusillus</em> (adults)</td>
<td>0.51</td>
<td>0.41</td>
</tr>
<tr>
<td><em>C. maculatus</em> (adults)</td>
<td>9.7</td>
<td>13.8(1.7)</td>
</tr>
<tr>
<td><em>T. variabile</em> (adults)</td>
<td>0</td>
<td>1.5</td>
</tr>
<tr>
<td>(larvae)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td><em>T castaneum</em> (adults)</td>
<td>0</td>
<td>2.7(3.8)</td>
</tr>
<tr>
<td>(pupa)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(larvae)</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>(eggs)</td>
<td>6.4(3.4)</td>
<td>1.3(0.9)</td>
</tr>
<tr>
<td><em>T. confusum</em> (adults)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(pupa)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(larvae)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(eggs)</td>
<td>0</td>
<td>2.4(1.0)</td>
</tr>
</tbody>
</table>

1 exposure 24 hr., temperature 28°C
2 mortality assessed at 24 hr after dosing

Adults of *R. dominica* and Psocid were the most susceptible to carbonyl sulfide, as 7.28mg/L concentration gave 100% mortality (Table 1). *O. surinamensis* and *C. chinensis* were less susceptible as 14.5mg/L gave 100% mortality. For 100% control of *S. oryzae*, *S. zeamais*, *L. serricorne*, *C. pusillus*, *C. maculatus*, *T. variabile* and *T. castaneum* 29.2mg/L was needed. *T. confusum* was tolerant to carbonyl sulfide, having 100% mortality only at 44.2mg/L. *T. castaneum* and *T. confusum* eggs and pupae were more tolerant to carbonyl sulfide than larvae and adults. The eggs of *T. confusum* were the most tolerant stage. Desmarcheler (1994) also found that the most susceptible species tested were adult Psocid and adult *R. dominica*. Zettler et al. (1997) also indicated that the egg and pupa stages of *T. confusum* were the least susceptible to carbonyl sulfide.

According to the above results, it could be considered that a dosage of 30mg/L and one day exposure time are enough to control the most insects tested, but it needs either a higher dosage or a longer exposure time for the control of the eggs of *T. confusum*.

### The Effect of Carbonyl Sulfide on Seed Germination

Seeds of wheat, paddy, maize, sorghum, barley, soybean and mung bean were placed in 500ml bottle and fumigated for 7 days at the dosages of 0, 25, 50, 100, 250 and 500mg/L at 30°C and aerated for 7 days. Germination was tested by standard method. There were 4 replicates for each treatment.
Table 2. Effect of carbonyl sulfide on the germination rate of seed (%).

<table>
<thead>
<tr>
<th>Seed</th>
<th>Concentration of carbonyl sulfide (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Wheat</td>
<td>98.5</td>
</tr>
<tr>
<td>Paddy</td>
<td>95.3</td>
</tr>
<tr>
<td>Maize</td>
<td>96.6</td>
</tr>
<tr>
<td>Sorghum</td>
<td>62.5</td>
</tr>
<tr>
<td>Barley</td>
<td>24.0</td>
</tr>
<tr>
<td>Soybean</td>
<td>95.5</td>
</tr>
<tr>
<td>Mung bean</td>
<td>90.8</td>
</tr>
</tbody>
</table>

Among the 7 tested seeds, the germination of soybean, mung bean, and wheat decreased when the dosage increased (Table 2). Soybean color changed from yellow to green after fumigation and as the dosage increased, the color change increased. The paddy seeds showed the lowest degree of germination at 100 mg/L among tested concentrations. It seemed that the change of carbonyl sulfide concentration had no adverse effect on sorghum germination, and on the contrary, the increase of carbonyl sulfide concentration tended to have a positive effect on barley germination. The results of wheat (Table 2) were unlike that showed by Desmarchelier (1994) as carbonyl sulfide had no adverse effect on the germination of wheat. Maybe there were no higher dosage treatments in his experiments. According to the results of this paper, it could be recognized that except for sorghum and barley, the tested species of seeds should not be treated by carbonyl sulfide fumigation in practice.

The Effect of Carbonyl Sulfide on Quality of Wheat and Paddy

Each treatment of 1 kg wheat or paddy was fumigated with carbonyl sulfide at the dosage of 0 g/m³, 50 g/m³, 100 g/m³ or 200 g/m³ separately in fumigation bottle at 100% packing rate at 30°C. After 7 days exposure and 187 days aeration in enamel tray at room temperature, the wheat was milled with Brabender mill. The obtained flour was used for determination of properties of dough by the Brabender farinograph and Brabender extensograph and for making bread and steam bread for taste test. Paddy was milled after 180 days aeration, and the rice obtained was used for determination of the water absorption of rice, expansion and iodine-blue value of cooked rice, and dry substance in rice cooking water and the taste test of cooked rice.

Carbonyl sulfide fumigation at all dosage rate reduced flour quality (Table 3). It reduced the consistency of dough, curve area of extensogram and the volume of bread. At the highest concentration, it also gave an unpleasant flavor to bread and steam bread even after 180 days aeration. Carbonyl sulfide had no obvious adverse effect on the water absorption of rice, expansion of cooking rice, iodine-blue of cooking rice and dry substance in rice cooking water, but it could also bring an unpleasant flavor to cooked rice if the fumigation dosage was higher than 100 g/m³.

Table 3. Effect of carbonyl sulfide fumigation on quality of wheat flour.

<table>
<thead>
<tr>
<th>Test using farinograph</th>
<th>Dosage (g/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test using extensograph</td>
<td>0</td>
</tr>
<tr>
<td>Bread test</td>
<td>568</td>
</tr>
<tr>
<td>Unpleasant flavor</td>
<td>No</td>
</tr>
<tr>
<td>Test after 1 day aeration</td>
<td>Volume (ml)</td>
</tr>
<tr>
<td>Unpleasant flavor</td>
<td>No</td>
</tr>
<tr>
<td>Test after half a year aeration</td>
<td>Unpleasant flavor</td>
</tr>
</tbody>
</table>

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Research on the Safety of Carbonyl Sulfide

Carbonyl sulfide is a kind of flammable gas. If it is used as a fumigant for stored grain fumigation, its flammability and the safety measure should be studied.

The experiments were conducted in PVC film sachets with a pipe for introducing the gas. A pair of electrodes was installed in the sachet for producing electric spark. A series of gas mixtures at different concentrations in the air, carbonyl sulfide and carbon dioxide were added to these bags. Then ignited it by an induction coil. Its combustion or explosion was observed. The results are illustrated in figure 1. In figure, the flammable region was inside the triangle area, outside of which was the safe region. The flammability gas concentration range of single carbonyl sulfide in the air was 12 - 29% and outside this range the gas mixture was not flammable. This data is very similar to the data of Sax and Lewis (1989). The introduction of carbon dioxide to the mixture of carbonyl sulfide and air reduced the flammability of the gas mixture. When the volume ratio of carbonyl sulfide: carbon dioxide was equal to 1:0.5, the gas mixture was not flammable. This result gives a possibility to ensure the safety when carbonyl sulfide is used as a fumigant for stored grain fumigation.

Fig. 1. Flammable region of gas mixture of carbonyl sulfide, air and carbon dioxide

Sorption of Carbonyl Sulfide in Grain Fumigation

Wheat, paddy and maize were fumigated in 500ml fumigation bottles at a 90% packing rate at 30°C and dosage of carbonyl sulfide was 100g/m³. After dosing, gas samples were taken out by syringe at different times. The concentration of carbonyl sulfide was analyzed by gas chromatography with flame photometric detector (sulfur filter), column 4m x 3.2 mm, front 2m packed with 30% dioctyl phthalate on Shimalite, other 2m packed with 25% polyethylene glycol 600 on Shimalite, column temperature 60°C.

Results showed that, carbonyl sulfide in wheat (moisture content 13.8%) decayed rapidly, and 3 days after dosing, its concentration could not be detected. In maize (moisture content 13.1%) it maintained 6 days. In paddy (moisture content 12.0%) it decayed slowly as the concentration lowered nearly to nil at the 9th day. In an empty bottle, the same dosage of carbonyl sulfide was added at the beginning time of the first 5 days, the concentration reduced from 100% to about 35%, but during the 5 - 15th days its concentration lowered to less than 5%. These results could be explained that decomposition of carbonyl sulfide was closely relative to the moisture content of environment. Carbonyl sulfide under in water vapor hydrolyzes to carbon dioxide and hydrogen sulfide (Ferm 1957). In the empty bottle, carbonyl sulfide reacted with the moisture in the bottle, and at the beginning it decayed rapidly, but after the moisture was exhausted, it decayed slowly.

Field Trails of Carbonyl Sulfide Fumigation to Control Insect Pests of Stored Grain

Field trials were conducted in No 27 Warehouse of Mongyong Grain Station of Pengzhou city in June, 1996. 250kg of wheat or paddy was stored in bamboo mat bins, covered with PVC plastic film sheets and sealed to the ground with dry sand. The dosages of carbonyl sulfide were 0 g/m³, 50 g/m³ and 100 g/m³ respectively. Every treatment was duplicated. Insects tested were S. zeamais, T. castaneum and R. dominica. One hundred adult insects were placed in nylon net sachets with a small amount of broken wheat. Before fumigation, the sachets with insects were just put under the top surface of the grain.
After 7 days exposure, the mortality of insects was assessed. After 24 hrs, samples were analyzed for COS residues by gas chromatography. The detected lowest concentration of carbonyl sulfide was 0.005 mg/kg, the recovery from wheat was 93.5% and 83.6% from paddy. An exposure time of 7 days at dosages of 50 – 100 g/m³ is enough for controlling adults of *S. zeamais*, *T. confusum* and *R. dominica* (Table 4). In experiments the lower dosage was 50 g/m³, so it could be reduced for the control of these insects in practice. There were no COS residues detected in any of the samples.

Table 4. Results of field trials

<table>
<thead>
<tr>
<th>Grain</th>
<th>Dosage (g/m³)</th>
<th>Mortality of insects (%)</th>
<th>Residue of COS in grain (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td><em>S. zeamais</em></td>
<td><em>T. confusum</em></td>
</tr>
<tr>
<td>Wheat</td>
<td>0</td>
<td>3.2</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Paddy</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

Summary

1. Carbonyl sulfide is effective to control many species of stored grain insect pests, among them *R. dominica* and Psocids are most sensitive.
2. Except sorghum and barley, carbonyl sulfide fumigation can reduce seed germination of the other grain tested. It also causes color change in soybean.
3. Carbonyl sulfide fumigation has adverse effect on the quality of flour and rice. It can bring an unpleasant flavor to the bread and cooked rice, even aerated for half a year.
4. Explosion of carbonyl sulfide in air is not violent. Adding carbonyl dioxide to the mixture of carbonyl sulfide, air can inhibit explosion and ignition of it.
5. Under field condition, carbonyl sulfide fumigation at a dosage of 50 g/m³ is effective to control insect pests of stored grain.
6. There are no COS residues in grain 1 day after the end of fumigation.
7. Carbonyl sulfide is not a good fumigant for controlling insect pests of stored grain, but it is worth studying its use in other fields as a fumigant.

References