

# Carbonyl sulphide as a fumigant for control of insects and mites

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## Abstract

The reasons why new fumigants are required are outlined. Principally, these reasons are actual or threatened withdrawal of use because of problems relating to mammalian toxicity or environmental protection. The properties of carbonyl sulphide (COS) as a fumigant are discussed.

Bioassay data are given for 11 species of insects, namely *Tribolium castaneum* (Herbst), *T. confusum* du Val, *Rhyzopertha dominica* (F.), *Oryzaephilus surinamensis* (L.), *Ephesthia cautella* (Walker), *Bactocera tyroni* (Froggart), *Lepidoglyphus destructor* (Schrank), *Coptotermes acinaformis* (Froggart), *Cryptotermes domesticus* (Haviland) and *Liposcelis bostrychophila* Badonnel.

All external stages were controlled by a 24-hour exposure to 25 mg/L, or by lower doses. The most susceptible stages were adult psocids and adult *R. dominica*; the most tolerant stages were eggs of *T. castaneum*, *O. surinamensis* and *E. cautella*. An exposure of 24 hours to 25 mg/L also controlled all internal stages of *R. dominica*. The hardest species to control was *S. oryzae*. Dosages required to control internal stages were examined for exposure periods of from 6 hours to 7 days, where single dosages were applied to infested wheat, and the grain held for different periods.

Chemical data on the sorption of carbonyl sulphide are compared with data from phosphine and methyl bromide. Levels of carbonyl sulphide in the intergranular air space decay more quickly than do levels of phosphine, but more slowly than do levels of methyl bromide. Carbonyl sulphide was blown through and out of a column of grain as easily as was phosphine, and was blown out of grain more easily than was methyl bromide. Carbonyl sulphide had no adverse effect on the germination of wheat.

Procedures for analysis by gas-chromatography are discussed. Carbonyl sulphide can be separated from other gases on packed columns or on wide-bore columns, but it lacks the specific sensitivity to at least one detector of fumigants such as phosphine or methyl bromide.

Data are presented on the chemistry of carbonyl sulphide and its environmental fate (each of which has been reviewed), and on its mammalian toxicity.

## Preamble

Fumigants are widely used for insect disinfestation of commodities, buildings and soils. No compound is ideal for use as a fumigant; for example, all are highly toxic to mammals and many are flammable. The use of many fumigants, including acrylonitrile, ethylene dibromide and ethylene oxide, has been stopped or restricted recently because of problems with human toxicity. Methyl bromide is under threat of restricted use, and possible withdrawal, because it apparently depletes

the ozone layer of the earth's atmosphere. There is, therefore, an urgent need for new fumigants. This paper discusses the properties of carbonyl sulphide with respect to its use as a fumigant. This usage has been patented by CSIRO (International Patent Application PCT/AU93/00018). One reason for patent protection is to increase the probability of the expenditure necessary for registration, as discussed in my keynote address on grain protectants at this conference.

This paper discusses the properties of carbonyl sulphide (COS) with respect to its use as a fumigant, under the following 8 headings:

1. the efficacy of carbonyl sulphide against insects and mites;
2. the chemistry and industrial uses of carbonyl sulphide;
3. the environmental fate of carbonyl sulphide;
4. mammalian toxicity of carbonyl sulphide and worker safety;
5. analysis and sorption of carbonyl sulphide;
6. movement of carbonyl sulphide through wheat;
7. the effect of carbonyl sulphide on seed germination; and
8. overview.

## The Efficacy of Carbonyl Sulphide against Insects and Mites

Insects tested were *Tribolium castaneum* (Herbst), *T. confusum* du Val, *Sitophilus oryzae* (L.), *Rhyzopertha dominica* (F.), *Oryzaephilus surinamensis* (L.), *Ephesthia cautella* (Walker), *Bactocera tyroni* (Froggart), *Lepidoglyphus destructor* (Schrank), *Coptotermes acinaciformis* (Froggart), *Cryptotermes domesticus* (Haviland) and *Liposcelis bostrychophila* Badonnel.

Bioassays for external stages were conducted in sealed glass jars, fitted with a Mininert valve. The humidity in the jars was 55–60%, except for assays on psocids and mites, where 5 g of 14% moisture wheat was added to jars, to raise the humidity to approximately 70%, and for assays with fruit fly, where 1 mL of water was added to each jar. Assays were performed in triplicate, using 30–50 insects and results discarded when control mortality exceeded 5%. After exposure periods of 6 or 24 hours, insects were placed on wheat for assessment of mortality 7 days after the end of dosing. Bioassays for internal stages of *R. dominica* and *S. oryzae* used cohorts aged 0–1 weeks, 2–3 weeks and 4–5 weeks. This was achieved by leaving 50 adults to oviposit for 1 week on 300 g of 11.8% moisture wheat at 25°C, removing adults and allowing to stand for the appropriate period (e.g. 2 weeks for assays on internal stages aged 2–3 weeks). Fumigant was added to 300 g of wheat in a 700 mL sealed glass jar. Assays on immature stages were replicated 6–9 times. The progeny were allowed to develop for 9 weeks after oviposition at 30°C, and assessed relative to control.

Results for external stages are summarised in Table 1 which records assay conditions, LC<sub>95</sub> values and 'minimum effective doses', i.e. the lowest tested dose that gave 100% mortality from at least 100 insects. All tested external stages were completely controlled by a 24 hour exposure to a dosage of 25 mg/L. The most susceptible species tested were adult

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psocids and adult *R. dominica*; the most tolerant stages were eggs of *T. castaneum*, *O. surinamensis* and *E. cautella*.

Results for internal stages of *S. oryzae* and *R. dominica* (including eggs) are summarised in Table 2. An exposure of 24 hours to dosages of 16–25 mg/L controlled all stages of *R. dominica* (100% mortality in 5/6 replicates). Eggs and adults of this species are also susceptible to carbonyl sulphide (Table 1). *S. oryzae* was harder to control than *R. dominica* (Table 2), and a 24-hour exposure to 24 mg/L a dosage that completely controlled *R. dominica*, controlled only an average of 80.7% of *S. oryzae*.

Both the dosage and period of exposure were varied in experiments on immature *S. oryzae*, and results are recorded in Table 2. Thus, a 6-hour exposure to a dosage of 200 mg/L gave 98.1% control of *S. oryzae*, whereas 100% control was obtained by a 24-hour exposure to a dosage of 60 mg/L, a 72-hour exposure to a dosage of 30 mg/L and an 168-hour exposure to a dosage of 20 mg/L. In the last example, measured concentrations of carbonyl sulphide fell from 17 mg/L 3 hours after dosing, to 7 mg/L, 168 hours after dosing.

In summary, a single dosage of 25 mg/L and an exposure period of 24 hours controlled the external stages of all tested insects and all stages, including internal stages, of *R. dominica*. However, control of internal stages of *S. oryzae* required either a higher dosage or a longer exposure period.

### The Chemistry and Industrial Uses of Carbonyl Sulphide

Pure carbonyl sulphide is a colourless, odourless gas with a boiling point of  $-50.2^{\circ}\text{C}$ . Its chemistry has been reviewed (Ferm 1957). Its vapour density at 1 atmosphere and  $25^{\circ}\text{C}$  is 2.485. Carbonyl sulphide, according to Ferm, is 'stable, but can undergo decomposition, hydrolysis, oxidation and reduction' and, as shown in Section 3, these reactions enable carbonyl sulphide to play a major, indeed almost certainly essential, role in the natural sulphur cycle in plants and soils.

Carbonyl sulphide has a water solubility of 1.4 g/L at  $25^{\circ}\text{C}$  (Kluczewski et al. 1985). At the same temperature, water solubilities of methyl bromide and carbon tetrachloride are, respectively, 13.4 g/kg and 0.28 g/kg (Worthing 1979). The solubility of phosphine is given by Fluck (1973) as 22.8 mL per 100 ml [0.35 g/L] at  $17^{\circ}\text{C}$ , based on the data of Weston (1954), but the original article covers a much wider range of temperatures.

Carbonyl sulphide has been extensively studied for a number of reasons, including its natural role in the sulphur cycle (cf Section 3), its presence in pyrolysis products, its use as a chemical feedstock (see e.g. Leiber and Berk 1985), its presence as radioactive carbonyl sulphide in releases from nuclear reactors cooled with carbon dioxide (Kluczewski et al. 1985), and its formation, in mammalian systems, in the metabolism of some sulphur-containing chemicals.

### The Environmental Fate of Carbonyl Sulphide

An important requirement of any fumigant is that it does not harm the environment. The environmental fate of carbonyl sulphide has been reviewed (Payton et al. 1978; Kluczewski et al. 1985; Mihalopoulos et al. 1989). It occurs uniformly in the troposphere at a concentration of  $1.3 \text{ g/m}^3$ . It has been suggested as the major natural sulphur species in the atmosphere. Emissions from natural and anthropogenic sources are estimated as being between 1 and 10 million tonnes per year (Mihalopoulos et al. 1989).

Ferm (1957) outlines preparation of carbonyl sulphide from S (sulphur),  $\text{CS}_2$  (carbon bisulphide) and KCNS (potassium thiocyanate), and reactions to form  $\text{SO}_2$  (sulphur dioxide),  $\text{SO}_4$  (sulphate),  $\text{H}_2\text{S}$  (hydrogen sulphide),  $\text{CS}_2$  (carbon bisulphide) and S (sulphur).

Carbonyl sulphide forms part of the natural sulphur flux, e.g. in soils (Staubes et al. 1989) and marshes (Stuedler and Peterson 1985). It is formed in the anaerobic degradation of manure and compost, and is suggested to be an intermediate in the bacterial sulphur cycle (Elliott and Travis 1973).

As an example of the natural flux of carbonyl sulphide, Stuedler and Peterson (1985) found an average yearly emission from a New England, USA salt marsh of  $34.3 \text{ g}$  of sulphur/ $\text{m}^2/\text{hour}$  (i.e.  $64.3 \text{ g}$  of carbonyl sulphide/ $\text{m}^2/\text{hour}$ ). A mean value of carbonyl sulphide flux from soils has been estimated as  $540 \text{ ngm}^2/\text{hour}$  (Mihalopoulos et al. 1989).

Taylor et al. (1983) studied decomposition velocities on plants, which took up carbonyl sulphide more slowly than they did sulphur dioxide, but more quickly than carbon disulphide. Carbonyl sulphide is less phytotoxic to bean plants (*Phaseolus vulgaris*) than sulphur dioxide or hydrogen sulphide (Taylor and Selvidge 1984). The estimated concentration by time product at which a decline in photosynthesis occurs is  $4.8 \text{ mg/hour/m}^3$ , at concentrations in the range  $0.36\text{--}4.9 \text{ mg/m}$ .

Mihalopoulos et al. (1989) showed that carbonyl sulphide levels in the atmosphere over land, as distinct from oceanic sites, increase with height above ground and postulate that plants act as a sink for carbonyl sulphide. Mihalopoulos et al. (1989) also summarise data on atmosphere levels, which do not appear to be rising, stratospheric photo-oxidation ( $0.1\text{--}0.16 \text{ Mt/year}$ ) and reaction with hydroxy radicals (slow; half life of about 17 years for typical concentrations of hydroxy radicals). Hoffman (1990) discusses the postulate that background sulphuric acid levels in the stratosphere are caused by 'a sulphur-bearing compound that is chemically inert and water-insoluble, such as carbonyl sulphide'.

It is clear that carbonyl sulphide is an intermediate — probably essential — in the atmospheric sulphur cycle. This in itself does not exclude the possibility of localised environmental problems from large-scale usage. Nitrate ion, for example, is an intermediate in the nitrogen cycle, but is also a major pollutant of aquifers. Nonetheless, fumigation with carbonyl sulphide is highly unlikely to cause non-localised environmental damage of the type caused by methyl bromide.

### Toxicity of Carbonyl Sulphide to Mammals and Worker Safety Aspects

A good fumigant should be safe to consumers and workers, and parameters such as flammability and acute and chronic toxicity are important.

Sax and Lewis (1989) summarise the properties of carbonyl sulphide and other chemicals. From these authors, carbonyl sulphide has a flammability range of 12–28.5%, V/V, in air. In comparison, the authors list the flammability limits of methyl bromide as 13.5–14.5%, those for phosphine as above 1%, those for carbon bisulphide as 1.3–50%, those for ethylene dichloride as 6.2–15.9% and those for ethyl formate as 2.7–13.5%. Thus, carbonyl sulphide is flammable, but insecticidal concentrations are well below the 'lower explosion limit'.

Sax and Lewis (1989) state that carbonyl sulphide is a 'poison by intraperitoneal route. Mildly toxic by inhalation, Narcotic in high concentration. An irritant'. A fatal accident with carbonyl sulphide, caused by high concentrations of carbonyl sulphide in an enclosed space, is discussed by Thies et al. (1968), who also give acute toxicity data on cats, rabbits

**Table 1.** Toxicity of carbonyl sulphide to insects and mites

Species	Stage	Exposure (hours)	Temperature (°C)	LC <sub>95</sub>	Minimum effective <sup>a</sup> dose (mg/hour/L)
<i>Rhyzopertha dominica</i>	adult	6	25	38	68.7
<i>Tribolium castaneum</i>	adult	6	25	82	101
	adult	24	25		297
<i>Sitophilus oryzae</i>	adult	6	25	99	100
	adult	24	25		264
<i>Oryzaephilus surinamensis</i>	adult	6	30	198	240
	adult	24	30		240
<i>Tribolium confusum</i>	adult	6	25	111	146
<i>Lepidoglyphus destructor</i>	adult	6	27		120
	adult	24			240
<i>Liposcelis bostrychophila</i>	adult	6	25		22.5
<i>Coptotermes acinaformis</i>	adult	24	30		288
<i>Coptotermes domesticus</i>	adult	6			360
<i>Tribolium castaneum</i>	pupae	6	30	290	360
	pupae	24	30	490	600
<i>Ephestia cautella</i>	pupae	24	27		240
<i>Bactocera tyroni</i>	pupae	6	27		360
	pupae	24	27	440	600
<i>Rhyzopertha dominica</i> <sup>b</sup>					
<i>Sitophilus oryzae</i> <sup>b</sup>					
<i>Coptotermes acinaciformis</i>	nymphs	24	27		600
<i>Tribolium castaneum</i>	larvae	6	25	270	300
	larvae	24	30	-	480
<i>Ephestia cautella</i>	larvae	6	30		240
	larvae	24	39	410	480
<i>Oryzaephilus surinamensis</i>	larvae	6	30	210	300
	larvae	24	30		360
<i>Bactocera tyroni</i>	larvae	6	27		180
	larvae	24	27		360
<i>Rhyzopertha dominica</i>	eggs 0-1 day	24	30	145	192
	eggs 0-1 day	6	30	102	144
	eggs 2-3 days	24	30		144
	eggs 4-5 days	24	30		120
<i>Tribolium castaneum</i>	eggs 0-1 day	24	30	520	600
		6	30	430	480
		48	30		360
<i>Oryzaephilus surinamensis</i>	eggs 0-1 day	24	30	495	600
		6	30	390	420
<i>Bactocera tyroni</i>	eggs -8h	24	30	460	600
<i>Ephestia cautella</i>	eggs 0-1d	24	30	450	600
		6	30		720

<sup>a</sup> The minimum tested dose that caused 100% mortality in assays against at least 100 insects.

<sup>b</sup> cf. experiments on internal stages, Table 2.

and guinea pigs. Klemenc (1943) reports data on mice. In these studies there was a cut-off point at which no effect was observed. This was a 6-hour exposure to 0.03%, V/V, in cats, rabbits and guinea pigs (Thiess et al. 1968) and indefinite exposure to 0.09%, V/V in rats (Klemenc 1943).

In a 7-week exposure of 50 ppm carbonyl sulphide to rabbits, Hugod (1981) and Hugod and Astrup (1981) concluded that carbonyl sulphide had no significant effect on myocardial ultrastructure. Chengelis and Neal (1979, 1980) showed that carbonyl sulphide is degraded by the enzyme carbonic anhydrase to hydrogen sulphide. This supports the previous classification of Thiess et al. (1968) that carbonyl sulphide, along with hydrogen sulphide and hydrogen cyanide, was an 'either-or' poison, meaning that recovery to exposure was complete, except where fatalities have occurred.

As carbonyl sulphide is a major contaminant of hydrocarbons, etc., much work has been done on its removal from air streams. The usual method involves an amine dissolved or suspended in a liquid scrubbing medium such as water or oil (Ferm 1957). Other scrubbers include ion-exchange resins and absorbent clays containing monoethanolamine (Ferm 1957). Thus, carbonyl sulphide scrubbing is already a commercial process which could be adapted to grain storage, if required.

### Analysis and Sorption of Carbonyl Sulphide

Procedures for analysis of standard concentrations are outlined by Ferm (1957). Carbonyl sulphide can be chromatographically resolved on packed columns (e.g. Tangerman 1986) or on capillary columns (e.g. Desmarchelier, these proceedings). It is relatively insensitive to the electron-capture and flame-ionisation detectors, but shows some selectivity to the flame photometric detector (sulphur mode) and the photo-ionisation detector. In each case, however, more carbonyl sulphide is required than carbon bisulphide to achieve the same machine response.

In addition to direct chromatographic analysis of carbonyl sulphide, Leiber and Berk (1985) report an in situ derivitisation procedure whereby carbonyl sulphide is trapped in polyamide impregnated with diamino propane. This method

**Table 2.** % control of all immature stages of *R. dominica* and *S. oryzae* from exposure to carbonyl sulphide at 25 °C

Species	Dosage (mg/L)	Exposure period (hour)	% mortality
<i>R. dominica</i>	8	24	93.1
	16	24	99.0
	25	24	99.96
		48	100
	45	24	100
<i>S. oryzae</i>	24	24	84.4
	200	6	98.1
	60	6	81.2
		24	99.8
		48	100
	40	48	100
	30	48	99.2
		72	100
	20	72	97.3
	20	168	100
10	168	75.0	

was used to detect air concentrations in the range 1–20 ppm carbonyl sulphide.

In fumigation, the amount of gas in the intergranular air space declines with time, even in sealed systems. The rate of disappearance of the fumigant is important for estimating the mean and range of concentrations over an exposure period.

Figure 1 compares the sorption of carbonyl sulphide, methyl bromide and phosphine on wheat. Carbonyl sulphide is much less strongly sorbed than methyl bromide, and slightly more sorbed than phosphine. Because the decay of carbonyl sulphide is relatively slow, concentrations that are able to affect insects are still present several days after initial dosage. This explains why the minimum effective dosage can be reduced by extending the exposure period (Section 1).

### Movement of Carbonyl Sulphide through Wheat

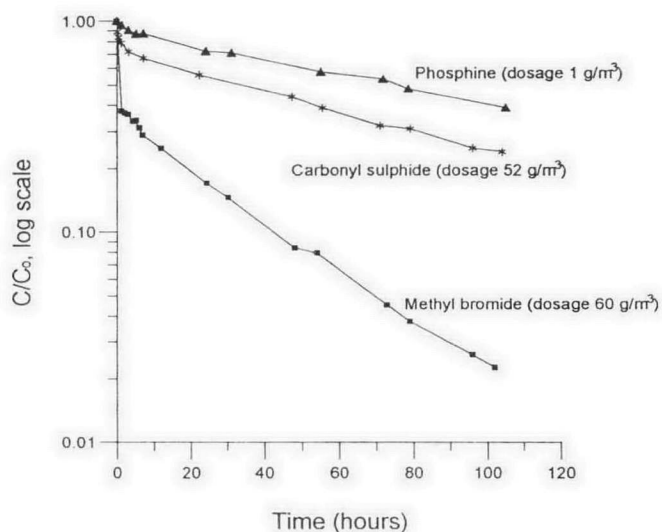
An ideal fumigant should be able to be easily passed through bulk grain, in order to obtain good distribution and in order to be able to blow away all fumigant after fumigation.

In a comparison between methyl bromide, phosphine and carbonyl sulphide, each fumigant (20 mL) was separately blown through a 1.1 m column of wheat, of total volume 7.9 L, at an airflow rate of 200 mL/minute. Each gas was introduced via a 200 mL flask at the bottom of the column. Concentrations in the eluate, at the top of the column, are recorded in Figure 2, for all concentrations greater than 1 ppm, V/V. The 'chromatography' of phosphine and carbonyl sulphide are essentially identical with respect to retention time, peak width and degree of tailing. However, methyl bromide has a broader peak and greater tailing, consistent with stronger sorption.

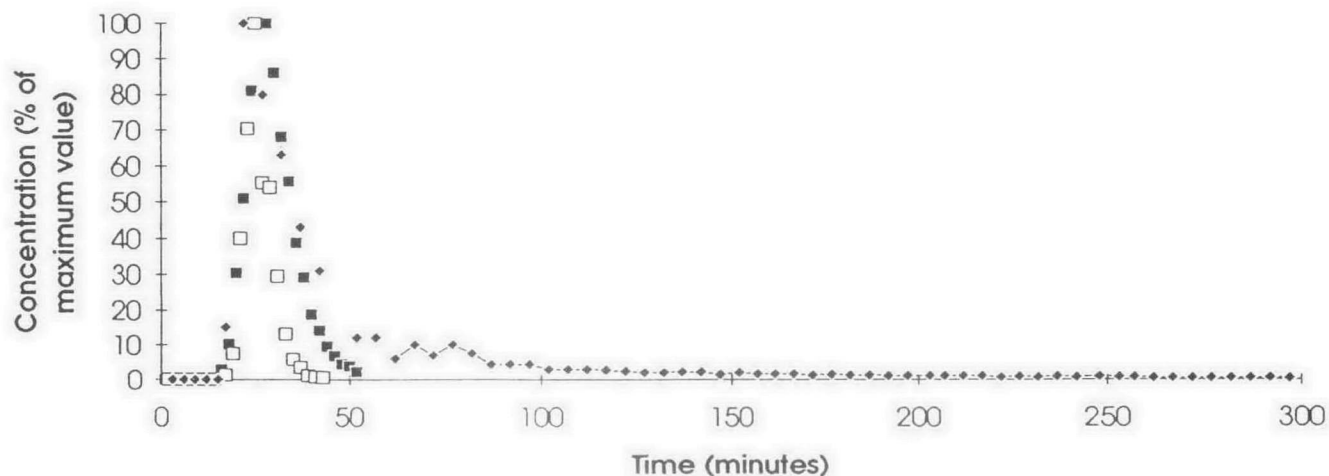
Note that carbonyl sulphide was rapidly blown out of a grain column, to levels below 1 ppm in the intergranular air.

### The Effect of Carbonyl Sulphide on Seed Germination

It is important that fumigants do not harm grain quality, and viability of seeds is an important quality test. Australian Standard White wheat was conditioned to 12 and 16% moisture, as determined by the ISO air oven method. Grains



**Fig. 1.** Comparative sorption data for phosphine, carbonyl sulphide and methyl bromide, taken from measurement of loss of fumigant concentrations in sealed containers 95% full of wheat of 12% moisture content, wet basis, at 25 °C.



**Fig. 2** Concentration of fumigant, (% of maximum concentration) eluting from a 1.1M column of wheat, at an air flow of 200mL/minute, plotted against time (in minutes). □: carbonyl sulphide; ■, phosphine; ◆, methyl bromide.

were dosed for 24 hours with concentrations of carbonyl sulphide of 0.5% V/V, 1.0% V/V and 5.0% V/V. Corresponding nominal concentration  $\times$  time products were 300 mg/hour/L, 600 mg/hour/L and 3000 mg/hour/L.

No adverse effect on seed germination was detected, either in tests immediately after dosing or 3 months later. Germination was slightly higher in treated wheat than in control wheat on 11/12 occasions.

### Overview

No fumigant is ideal, and most suffer at least some problems in areas of worker safety, flammability, residues and the environment. Carbonyl sulphide is no exception to this rule, but it has qualities that make it comparable with fumigants such as methyl bromide and phosphine. For example, its flammability limits are greater than those of methyl bromide but less than those of phosphine. It is environmentally superior to methyl bromide and, on the basis of greater knowledge, to phosphine. Phosphine is the best fumigant for long exposures, methyl bromide is the best for short exposures, but carbonyl sulphide is versatile being able to be used for short exposures, or for longer exposures at reduced dosages.

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