# COMMERCIAL POTENTIAL OF METHYL BROMIDE AND CARBON DIOXIDE MIXTURES FOR DISINFESTING GRAIN

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ABSTRACT

The commercial potential of methyl bromide and carbon dioxide gas mixtures, under recirculation, for grain insect control was investigated in a trial in a 2000 t welded steel silo. The trial aimed to achieve a *Ct*-product of 50 g/h/m$^3$ of methyl bromide in an atmosphere of 20% or more of carbon dioxide within 24 h. This is one third of the minimum recommended *Ct*-product for application of methyl bromide alone. Where the desired *Ct*-product or higher was achieved in an atmosphere containing 40-60% carbon dioxide all stages of *Tribolium castaneum*, *Rhyzopertha dominica*, *Sitophilus oryzae* and *S. granarius* were killed. The trial further indicated that bromide residues on grain can be reduced by at least two-thirds as a consequence of using a lower concentration of methyl bromide.

## INTRODUCTION

Laboratory studies on the effects of mixtures of methyl bromide and carbon dioxide on insects have indicated that the toxicity of methyl bromide can be increased in the presence of carbon dioxide (Cotton and Young, 1929; Jones, 1938; Bond and Buckland, 1978).

More recently laboratory experiments by Williams (1982) demonstrated that the methyl bromide concentrations required to kill adults of the stored grain beetles *Sitophilus oryzae* (L.), *Rhyzopertha dominica*, (F.) and *Tribolium castaneum* (Herbst) can be reduced by a factor of less than 2 when the fumigant is used in conjunction with an atmosphere containing 20% or more of carbon dioxide in 24 h fumigations. Such gas combinations were effective under a wide range of temperatures and relative humidities. Further experiments demonstrated similar effects with immature stages of the beetles. Tests in 15 t wheat silos indicated that a dosage of 5 g/m$^{-3}$ of methyl bromide (5 x lower than the standard recommended dose) in an atmosphere containing 20% or more of carbon dioxide, under continuous recirculation for 24 h, would control grain insects.

Calderon and Carmi (1973) carried out commercial trials with gas mixtures in which methyl bromide (liquid at 50 g/m$^3$) in conjunction with carbon dioxide (dry ice at 250 g/m$^{-3}$) was applied to the surface of grain in silos for insect control. Gas distribution depended on gravity and convection currents within the silos, with a minimum treatment time of 96 h for disinfestation. This treatment avoided the use of gas recirculation but required a higher dosage of methyl bromide and longer treatment time than for use of recirculated methyl bromide (Monro, 1969).

This paper describes a commercial trial, at Sanger in southern New South Wales, in which the effectiveness of methyl bromide in conjunction with carbon dioxide, under recirculation, was compared with a similar concentration of methyl bromide applied alone.

## MATERIALS AND METHODS

### *Experimental Silo*

A silver-painted, welded steel cylindrical silo (2000 t) with a conical roof welded to its walls was used for the trial. The silo had a concrete floor with a central opening for grain discharge and a Y-shaped perforated metal aeration duct. To guard against gas leakage the wall-to-floor joint was sprayed with a polyvinyl chloride resin formulation (Envelon). The outloading gate valve was treated with molten beeswax which set to form a seal that later could be readily broken to allow grain to be outloaded. A hinged steel plate lined with foam rubber was made to seal the manhole at the top of the silo. A pressure decay test (Banks and Annis, 1977) was carried out prior to fumigation and soap solution used to check for leaks. Leaks found were sealed with silicone rubber. Silo dimensions and details of the load are given in Table 1.

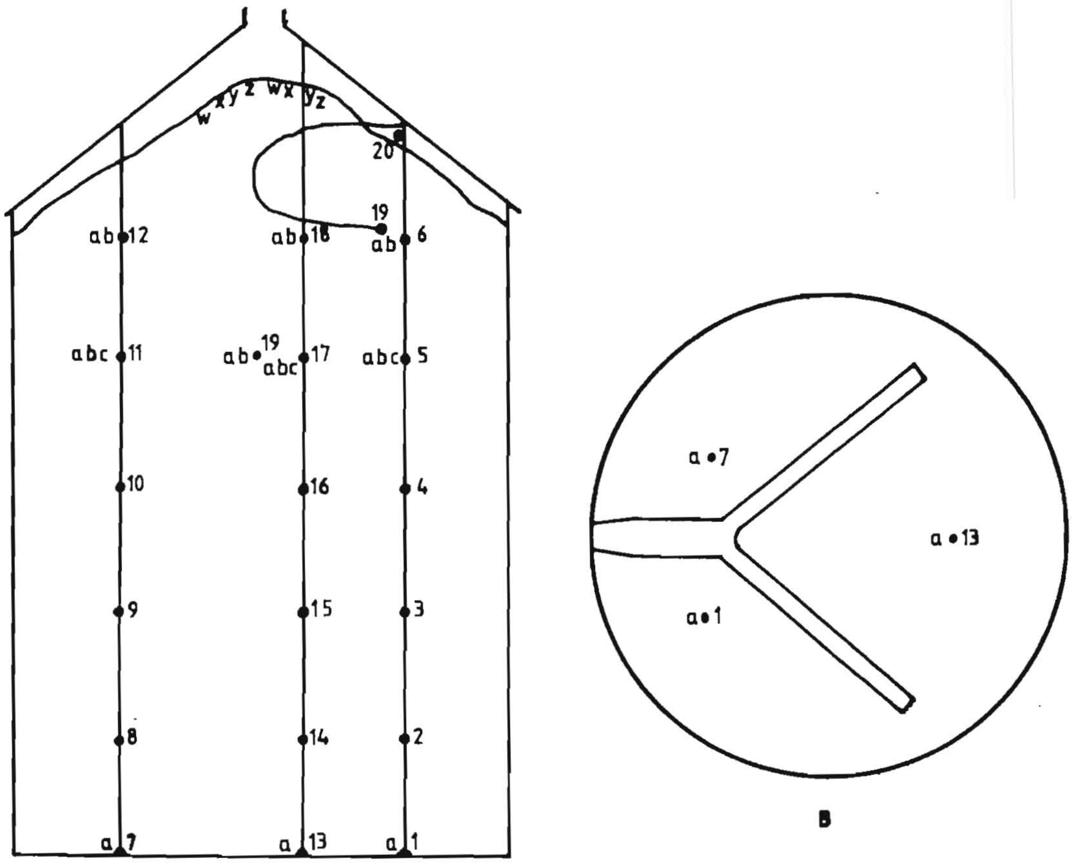
### *Monitoring Physical Conditions*

Gas concentrations within the silo were sampled periodically from 20 locations (Fig. 1) using 4 mm (i.d.) semi-rigid nylon sampling lines attached to steel cables. Carbon dioxide concencentrations were measured by a thermal conductivity detector (Gow-Mac Portable Gas Analyser, Model 20-602) which sampled directly from the gas stream drawn through the gas lines by an electric pump. Methyl bromide concentrations were measured by taking 100 micro litres samples from the gas lines and injecting them into a Packard 427 Gas Chromatograph fitted with F1D detectors and dual glass columns 1.5m x 2mm (i.d.) packed with Ucon oil (LB 550X) on Chromsorb W. HP. (60-80 mesh). Chromatograph temperatures were 60°C for the oven and 80°C for both the injection ports and detector block.

Ambient temperature and the grain temperatures at the gas sampling locations were monitored using a multi-point recorder (recording systematically from each point every 15 minutes). Grain moisture content was measured by determining the loss of weight on drying 2 g of ground wheat for 1 h in a ventilated oven at 130°C. Bromide levels in the wheat before and after fumigation were determined by X-ray fluorescence techniques (see Table 1).

Table 1.
Experimental Data

| | |
|---|---|
| Silo dimensions | |
| Height to eaves | 17.6 |
| Height of cone | 4.0m |
| Diameter | 13.9m |
| Volume | 287$m^3$ |
| Load | |
| Grain | ASW grade wheat |
| Moisture content on intake | 10.7% wet basis |
| Mass | 2367t |
| Height of head space | 1m |
| Volume of head space | 50$m^3$ |
| Load space | 2822$m^3$ |
| Estimated intergranualar volume (assuming 40% porosity) | 1129$m^3$ |
| Total gas volume | 1179$m^3$ |
| Average grain temperature | |
| - during experiment 1 | 31.7°C (13 -44.8°C) |
| - during experiment 2 | 30.0°C (10 - 23.5°C) |
| Average ambient temperature | |
| - during experiment 1 | 19.2°C (13 - 31.0°C) |
| - during experiment 2 | 15.9°C (10 - 23.5°C) |
| Insect species infest grain | R. dominica<br>T. Castaneum<br>Oryzaephilus surinamensis |
| Bromide levels on grain | |
| from surface before fumigation | 8 ± 0.5 ppm |
| from surface after experiment 1 | 9 ± 1.0 ppm |
| from surface after experiment 2 | 12 ± 0.7 ppm |
| from location 13 after experiment 1 | 13 ± 0.7 ppm |
| from location 13 after experiment 2 | 15 ± 0.5 ppm |




A B

Figure 1.

A. Diagram of silo showing locations of gas sampling lines, thermocouples and insect cages.

B. Configuration of aeration duct and location of sampling points and insect cages on the silo floor.

- 1-20 Locations of gas sampling points and thermocouples.
- 19* Intended location of point 19 gas line and thermocouple.

| Spear Cage | Pipe Cage | Insect Species |
|---|---|---|
| a | w | T. castaneum |
| b | x | R. dominica |
| c | y | S. granarius |
| | z | S. oryzae |

*Bioassays*

Two types of insect cages were placed in the grain; spear shaped stainless steel cages 240mm long and 37mm in diameter fitted with steel gauze panels, and polyvinyl chloride pipe cages 75mm high and 167mm in diameter the ends of which were covered with steel gauze. The spear cages were probed into the grain, some being positioned during filling of the silo. The spear cages at the base of the silo were introduced via steel pipes 3.6m long and 51mm (i.d.) welded to the silo wall with 3.44m projecting inside the silo. The pressure of wheat at the ends of these pipes was so great that only the spear tips of the cages could be pushed into the wheat. The pipe cages were placed in the wheat just under the surface of the bulk at the top of the silo. Locations of the cages are shown in Fig. 1.

The bioassay insects were *T. castaneum* (strain CTC 12), *R. dominica* (CRC 118), *S. oryzae* (CSO 231), and *S. granarius* (VSG 24). All strains except VSG 24 were insecticide resistant. The cages each contained a single insect species, the spear cages for *T. castaneum* held 60 g of wheat and 10 g of breeding medium (wholemeal flour and yeast) containing an undetermined number of eggs, to which were added 200 adults (2-4 weeks old), 50 mature larvae and 50 young pupae. Spear cages carrying *R. dominica* and *S. granarius* held 70 g of wheat containing immature stages and 200 adults (2-4 weeks old).

Pipe cages carrying *T. castaneum* held 950 g of wheat and 50 g of wholemeal flour containing an undetermined number of eggs, to which were added 500 adults (2-4 weeks old), 50 mature larvae and 50 pupae. The pipe cages for *R. dominica* and *Sitophilus* spp. held 1000 g of wheat containing immature insects and 500 adults (2-4 weeks old).

*Gas Recirculation System*

The silo was fitted with rigid 0.23 m (i.d.) polyvinyl chloride piping for gas recirculation. Piping carried gas from a Richardsons E6118 fan (fitted with a 1.1 kW 3 phase motor and rated at 310 $Ls^{-1}$, 0.75kPa, 2940 rpm, 0.52 kW at 21$^{o}$C) to the aeration duct in the silo and collected gas for recirculating from the headspace. The fan gave an air change in about 80 minutes. The top of the recirculation duct was fitted with a hinged steel cap which was opened after fumigation to assist ventilation. The base of the duct was fitted with a water filled pressure safety valve (minimum pressure 0.75 kPa).

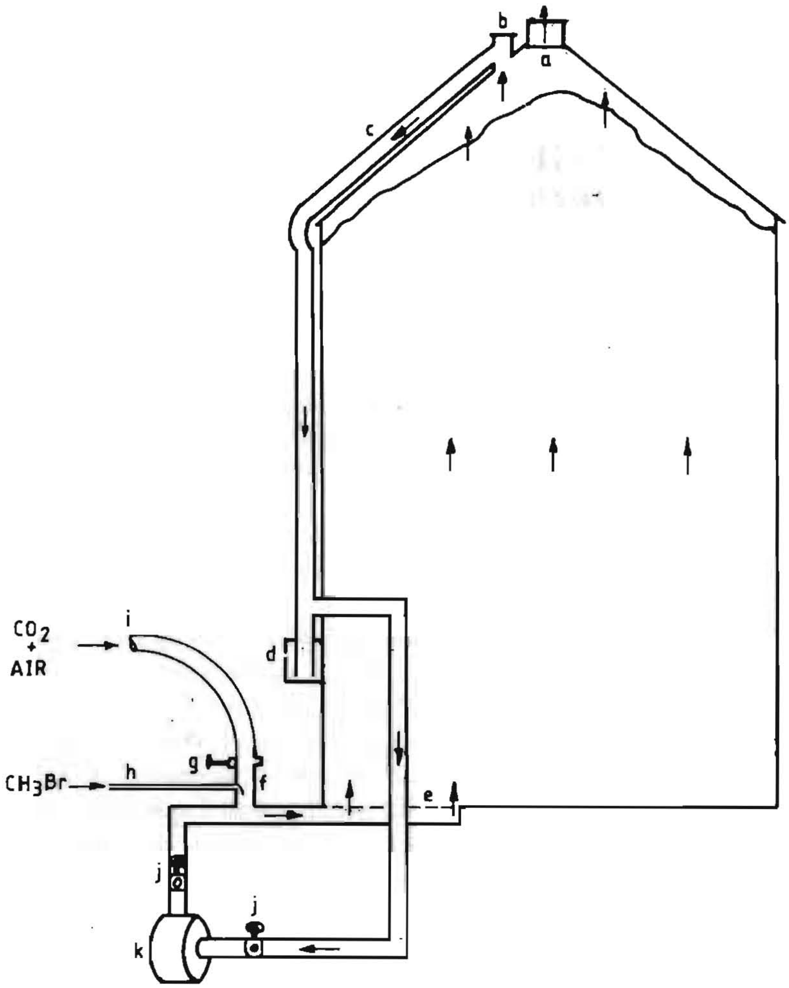



Figure 2.
Diagram of silo showing gas input and recirculation systems

a. manhole sealing plate,
b. cap on recirculation duct,
c. recirculation duct,
d. safety valve,
e. aeration duct,
f. steel pipe,
g. gate valve,
h. methyl bromide hose,
i. carbon dioxide hose,
j. ball valve,
k. gas recirculation fan.

### *Gas Introduction*

It was decided to modify the carbon dioxide application technique developed by Wilson *et al.* (1980) so as to introduce a methyl bromide and carbon dioxide mixture into the silo. On the basis of laboratory and small scale field trial results, Williams (1982), it was decided to aim at obtaining a *Ct*-product of 50 $g/h/m^{-3}$ of methyl bromide in an atmosphere containing 20% or more carbon dioxide in 24 h.

*Experiment 1*

Carbon dioxide was provided from a road tanker (4 t) connected to a vapouriser capable of delivering up to 3 t $h^{-1}$. The vapouriser was set to produce a 60% carbon dioxide in air mixture. This mixture was heated to 30°C (range 29.0 - 20.5°C) in the vapouriser and passed through a flexible steel hose 75mm (i.d.) coupled to a pipe at the base of the silo. The gas then passed through an open gate valve, below which a copper pipe 10 mm (i.d.) carried methyl bromide into the gas stream. The methyl bromide was dispensed from a cylinder, placed on scales (minimum graduation 0.1 kg) to measure dosage, through a dispenser and a vapouriser connected to a semi-rigid nylon hose leading to the copper pipe at the base of the silo.

The carbon dioxide and air mixture was introduced into the silo for a period of 10 min. Methyl bromide was then gradually added to the gas stream. During the purge air escaped from the headspace via the gas return duct to the recirculation fan which was connected to the fan after completion of the purge. Purging was stopped and the bin sealed when the carbon dioxide level in the headspace reached 20%. By the time this was done the carbon dioxide level in the headspace had risen to 60%. The purge lasted 63 min. during which 1.71 t of carbon dioxide and 8 kg of methyl bromide were introduced into the silo.

On completion of the purge the manhole cover and the gate valve on the gas delivery pipe were closed, the gas return duct to the recirculation fan was connected to the fan and the valves on either side of the recirculation fan were opened and the fan was started. Gas was recirculated for 24 h during which a further 8 kg of methyl bromide was introduced (4 kg after 6 h and another 4 kg after 12 h) to enable the desired *Ct*-product to be achieved. After 24 h the fan was turned off, the manhole cover and the cap on the recirculation duct opened, the valve on the gas intake side of the fan was closed and the pipe disconnected from the fan. The fan was then restarted and used to ventilate the silo for 15 h after which the methyl bromide level was below 15 ppm and grain could be safely handled.

*Experiment 2*

Experiment 2 was carried out in a similar way, but methyl bromide was applied alone without $CO_2$, into the recirculation duct and distribution by the recirculation fan. The dosage applied was exactly the same and was applied at the same time intervals as in experiment 1.

Table 2.

Cumulative products ($ghm^{-3}$) for methyl bromide at different sampling locations within the silo.

| Sampling Location | Cumulative *Ct*-Product for Methyl Bromide Experiment 1 with carbon dioxide | Experiment 2 with Methyl bromide alone |
|---|---|---|
| 1 | 61.1 | 76.2 |
| 2 | 56.4 | 71.4 |
| 3 | 62.0 | 56.9 |
| 4 | 60.4 | 59.8 |
| 5 | 62.7 | 35.3 |
| 6 | 51.0 | 32.0 |
| 7 | 63.1 | 80.5 |
| 8 | 63.5 | 78.7 |
| 9 | 52.9 | 55.1 |
| 10 | 62.0 | 49.9 |
| 11 | 59.1 | 35.5 |
| 12 | 46.3 | 30.7 |
| 13 | 61.9 | 26.0 |
| 14 | 55.8 | 44.2 |
| 15 | 67.6 | 40.8. |
| 16 | 57.1 | 34.8 |
| 17 | 54.1 | 34.6 |
| 18 | 38.2 | 36.4 |
| 19 | 47.1 | 37.8 |
| 20 | 25.0 | 3.5 |
| Totals: | 1107.3 | 900.1 |
| Average: | 55.4 | 45.0 |

## RESULTS

### *Grain Condition*

The grain moisture content, temperatures and bromide levels are given in Table 1. Grain temperatures of 35°C and over in the central region of the silo were probably due to an insect infestation in the wheat prior to fumigation. The bromide levels after experiment 1 were under two-thirds of those to be expected after a normal methyl bromide fumigation (Monro, 1969).

### *Gas Distribution*

The carbon dioxide assisted greatly in achieving even distribution of methyl bromide in the grain, much better distribution being obtained than in the comparison trial, experiment 2, where the methyl bromide without $CO_2$ was distributed by the recirculation fan (Table 2). This was most noticable at location 13 (Fig. 1) at the base of the silo in between the arms of the Y-duct where slow gas distribution had been expected because of pressure equalisation created by the gas flow from each duct arm. Carbon dioxide levels were maintained at 40-60% at all locations throughout the recirculation period.

### *Bioassays*

In experiment 1 insects in the spear cages at locations 5, 6, 11, 12, 17, 18, and 19 (see Fig. 1) were exposed to *Ct*-products of 38.2 - 62.7 g/h/m$^{-3}$ of methyl bromide and all were killed. Gas flow to the insect cages at the base of the silo (locations 1, 7 and 13) was restricted, especially in cage 13 where the pipe carrying the cage was exposed to the sun and air pressure within the pipe would have further restricted ingress of methyl bromide and carbon dioxide. In this cage 96% of adults and 57% of larvae survived but in the other cages all insects were killed.

In the pipe cages under the grain surface where the *Ct*-product could have been as low as 25 g/h/m$^{-3}$ all insects were killed, excepting 2 mature larvae or pupae of *S. oryzae* and 165 mature larvae and pupae of *S. granarius* which were reared to the adult stage by incubation of the grain.

At the end of experiment 1 a 1 kg grain sample from the surface was examined for insects and all were found to be dead.

In experiment 2 most caged insects at all locations survived.

## DISCUSSION

This study has demonstrated that methyl bromide and carbon dioxide gas mixtures under recirculation can provide effective insect control with a *Ct*-product of 50 g/h/m$^{-3}$ of methyl bromide in an atmosphere of 40-60% carbon dioxide. This *Ct*-product is one third of the minimum recommended for use of methyl bromide alone. It was ineffective when applied without carbon dioxide under the trial conditions.

Carbon dioxide was shown to be an efficient carrier for the methyl bromide and ensured good gas distribution during the purge. Distribution of methyl bromide alone by the gas recirculation fan was not as good. The gas distribution obtained by the purge may best be maintained by recirculating gas from the base of the silo to the headspace with a small fan in the manner used for carbon dioxide treatments (Wilson *et al.*, 1980). A further trial using this recirculation system is planned.

The low methyl bromide concentrations observed in the headspace are believed to have resulted from a combination of sorption of methyl bromide during its passage through the grain, gas leakage around the recirculation duct at the top of the silo and the recirculation fan sucking air into the silo through the leaks. Thus the trial indicated the importance of effective silo sealing for fumigations. The problem of low concentrations of methyl bromide in the headspace should be overcome by sealing the leaks at the top of the silo, by increasing the methyl bromide input to about 20-25 kg, and by reducing the recirculation rate and recirculating gas from the base of the silo into the headspace. Bromide residue levels would still be expected to be about two-thirds of those to be expected from a normal methyl bromide fumigation.

Costs of the methyl bromide and carbon dioxide treatment were estimated to be similar to those incurred for carbon dioxide alone (about 30 ¢ $t^{-1}$ for gas and labour). Advantages of using the methyl bromide and carbon dioxide gas mixtures are the short treatment time compared with that required for carbon dioxide alone and the reduced bromide residues on grain compared with those for methyl bromide alone.

## ACKNOWLEDGEMENTS

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## REFERENCES

Banks, H. J. and Annis, P. C. 1977
Suggested procedures for controlled atmosphere storage of dry grain. C.S.I.R.O. Aust. Div. Entomol. Tech. Pap., No. 13.

Bond, E. J. and Buckland, C. T. 1978
Control of insects with fumigants at low temperatures: toxicity of fumigants in atmospheres of carbon dioxide. J. econ. Ent., 71: 307-309.
Calderon, M. and Carmi, Y. 1973
Fumigation trials with a mixture of methyl bromide and carbon dioxide in vertical bins. J. stored Prod. Res., 8: 315-321.
Cotton, R. T. and Young, H. D. 1929
The use of carbon dioxide to increase the insecticidal efficacy of fumigants. Proc. Ent. Soc. Washington, 31: 97-102.
Jones, R. M. 1938
Toxicity of fumigant - $CO_2$ mixtures to the red flour beetle. J. econ. Ent., 31: 298-309.
Monro, H. A. U. 1969
Manual of fumigation for insect control. (2nd edition, revised) F.A.O. Agric. Stud. No. 79, 381 pp.
Williams, P. 1982
Methyl bromide and carbon dioxide mixtures for control of insect pests of stored grain. Proc. 1st Aust. Stored Grain Pest Control Conf., Melbourne, Section 5: 11-15.
Wilson, A. D., Banks, H. J., Annis, P. C. and Guiffre, V. 1980
Pilot commercial treatment of bulk wheat with $CO_2$ for insect control: the need for gas recirculation. Aust. J. Exp. Agric. Anim. Husb., 20: 618-624.