

## FUMIGATION TRIALS WITH A MIXTURE OF METHYL BROMIDE AND CARBON DIOXIDE IN LARGER TYPE SILO BINS

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### ABSTRACT

Tests with mixtures of methyl bromide and carbon dioxide for the control of stored product pests were conducted in silo bins at three sites. Very high methyl bromide concentrations and complete kill of insects were obtained when the CO<sub>2</sub> was applied as a gas. Where the CO<sub>2</sub> was applied as snow, and where it was applied as dry ice, the methyl bromide concentrations were much lower, and there were distinct areas where very low concentrations and some insect survival occurred.

It was concluded that air was trapped under the heavy gases, and that there may still be a need for recirculation to disperse methyl bromide more uniformly and thus ensure successful fumigation.

### 1 INTRODUCTION

The development by Calderon and Carmi (1973) of a method to fumigate grain successfully with methyl bromide in vertical silo bins without recirculation systems, by applying it as a mixture with CO<sub>2</sub>, has aroused considerable interest in the South African grain industry, because (i) a relatively cheap fumigant can be used, (ii) treatment can be applied to silos that lack recirculation systems, and (iii) the grain need not be turned, resulting in lower running costs for the silo, a saving of time, and less breakage of grain. However, Calderon and Carmi tested their method in bins of only 240 and 400 m<sup>3</sup> capacity, while many South African bins have internal volumes of over 5000m<sup>3</sup>. Furthermore, these authors conducted their tests in bins containing wheat, while the main South African crop is maize. In this respect it is interesting to note that Philips (1957) found little difference between wheat and maize in their resistance to airflow, but hardly any gravity penetration of methyl bromide into either commodity. Calderon and Carmi's main finding was that CO<sub>2</sub> assisted penetration of methyl bromide to the bottom of high vertical bins containing wheat. In contrast, Smit, Nolte and Brunnekreft (1959) obtained a complete kill below 15.2 m and no significant kill in the upper 1.5 m of maize in a bin of 27.4 m height where methyl bromide alone was injected with compressed air at points 0.0; 9.1 and 18.3 m below the grain surface. Thus it seemed justified to evaluate Calderon and Carmi's method under local conditions. Three tests were conducted, the

first in a relatively small silo bin of about  $1000\text{m}^3$  capacity at Settlers, and the other two in silo bins of over  $5000\text{m}^3$  at Driefontein and Bloekomspruit respectively. The results of these trials are presented here.

## 2 PROCEDURE

### 2.1 The Settlers Trial

The Settlers grain silo consists of two adjacent rows of nine cylindrical flat-topped concrete bins with star bins between them. The silo is equipped with a recirculation system for fumigation with methyl bromide and the bins are considered to be reasonably gastight (but see discussion). No test for gastightness was carried out and no sealing was done. The cylindrical bin in which the test was done (see Table 1) contained sorghum seed (m.c. 12-12.6% wet basis), naturally infested with various pest species (Table 2). Gas sampling tubes were placed as shown in Fig. 1. Carbon dioxide was applied as a gas from pressurised steel cylinders into the head space, and methyl bromide as a liquid on the grain surface. During application, care was taken not to exceed a pressure of 2.5 kPa. in the headspace.

During fumigation, gas samples were taken at intervals, and the concentration of methyl bromide was determined subsequently in the laboratory by GLC.

Two weeks after gas introduction, grain samples from the bin were again screened for live insects. The samples were then incubated for seven weeks at  $26^{\circ}\text{C}$  and 70% RH and checked for adult insects that developed from surviving eggs and pupae.

### 2.2 The Driefontein Trial

The Driefontein silo consists of free-standing concrete bins with conical concrete roofs. The dimensions and contents of the bins are given in Table 1. These bins are self-emptying through three grain outlets in the bin floor. The empty test bin was superficially sealed by applying putty to obvious crevices at the grain outlets and the inspection hatches in the wall near the bottom of the bin. The manhole and grain inlet were similarly sealed after the bin was filled with maize. No test for gastightness was carried out. Maize, infested with *Tribolium castaneum* and *Cryptolestes* sp., was transferred into it from another bin. Infestation levels and grain temperatures in the first bin are summarised in Table 3. During filling, the grain flow was stopped from time to time and cages containing food and all life stages of various pest species were placed in the test bin as shown in Fig. 2. The pest species concerned are listed in Table 4. Gas sampling tubes were placed at the same time, also shown in Fig. 2. The topmost cages were about 1 m below

the grain surface, which was about 4.5 m below the bin roof, as insufficient maize was available to fill the bin to capacity. The grain inlet and manhole were then sealed and CO<sub>2</sub> and methyl bromide were applied (Table 1). The pressure inside the bin was monitored on water manometers connected to the gas sampling tubes, and also in the headspace. Gas samples were taken 1h, 24h and 48h after treatment and the gas concentrations (CO<sub>2</sub> and CH<sub>3</sub>Br) were determined in the laboratory by GLC. After 7 days, emptying of the bin was started so that the insect cages could be retrieved. This was completed in about a week and the mortality of each species in each cage was then determined. While the bin was being emptied, two 25-kg samples were taken each day from the conveyor belt and examined for surviving insects from the natural infestation. A total of 10 such samples were taken.

The average mortality of all five species of the insects that were exposed in the cages was calculated and categorized into five groups. This data was analysed by Symap computer programs (Dougenick and Sheehan, 1975) and correlated with the distribution of methyl bromide gas on two vertical planes through the centre of the bin (N-S and E-W).

### 2.3 The Bloekomspruit Trial

The bins at the Bloekomspruit silo are almost identical to those at Driefontein (Table 1). The test bin here was prepared in the same way as the Driefontein bin except that there were ten levels in the grain bulk at which insect cages were placed (Fig. 3) and the cages contained only malathion resistant strain of *T. castaneum* and food. Five gas sampling tubes were placed at every alternative level on a N-S line across the bin (Fig. 3). Temperature cables were placed at a few points in the upper half of the grain bulk.

CO<sub>2</sub> and methyl bromide were applied as shown in Table 1.

At intervals after gas application the concentration of methyl bromide was determined, using a Miran 1A infrared gas analyzer. Gas readings were again grouped into 5 categories and subjected to Symap analyses to determine the probable gas distribution on the N-S vertical plane. The last readings were taken 110h (4.5 days) after the gases were applied. Emptying was then started and continued haphazardly over 5 weeks before completed and all insect cages were retrieved. Insect mortalities were only then determined.

## 3 RESULTS AND DISCUSSION

### 3.1 Settlers

The concentrations of methyl bromide gas at the top, middle and bottom of the bin at different intervals after application are shown in Fig. 4. For most of the time, the gas concentrations increased with depth, contrary to

Calderon and Carmi's results, where the highest methyl bromide concentrations were always found near the grain surface. Our results during this test seem to agree with that of Smit *et al.* who obtained the highest kill of test insects in the bottom part of the bin. It is unlikely, however, that the differing of the contents of the various bins contributed to these contradicting results. In our test, the bin contained tightly packed sorghum with about 37% interkernel space (Jay, 1971) which must be very similar to the interkernel space of the wheat in the Israeli bins. (35.8 to 36.2% for tightly packed wheat of different varieties and moisture contents - Jones, 1943): The bin used by Smit *et al.*, on the other hand, contained flat white maize with perhaps 45 to 50% interkernel space. Smit *et al.* concluded that the heavy gas apparently sank through the grain too quickly to give a satisfactory kill at the top of the bin and in a cone-shaped space below the manhole. In their test, no CO<sub>2</sub> was used as a carrier for methyl bromide. In our test, comparatively high methyl bromide concentrations were found generally. At the top, where concentrations were lowest, the calculated CT-product over 192 hours was 4649g h m<sup>-3</sup>, compared to 1890 (over 120h) and 2489g h m<sup>-3</sup> (over 96h) recorded by Calderon and Carmi at Rehovot and Brurim respectively (average concentrations 24.2, 15.7 and 25.9 g m<sup>-3</sup> methyl bromide respectively).

No surviving insects were found after fumigation, but, as will be seen later, this is not conclusive evidence that some insects might not have survived the treatment in certain parts of the grain bulk in spite of the high gas concentrations recorded at the three sampling points.

The Settlers bin was not gastight at all. Tests with a halide detector lamp revealed considerable leakage of methyl bromide underneath the concrete roof to adjacent bins and also some leakage at the grain outlet.

### 3.2 Driefontein

The numbers of insects at different depths in the bin from which maize was transferred for the test are given in Table 3. The heaviest infestation occurred at the grain surface. However, during transfer these insects would undoubtedly have been dispersed. The highest temperatures occurred in the centre of the grain bulk, but warmer and cooler grain would also have become mixed during the transfer operation. On the whole, the grain temperature was comparatively high for maize (which is normally around 20°C), no doubt as a result of the insect infestation.

The pressures inside the bin during treatment are given in Table 5. The build-up of pressure during this time indicates that the bin was quite gastight especially if the size of the bin and the moderate gas flow rate of 6.8 kg/min (ca. 3.7 m<sup>3</sup>/min.) are taken into consideration.

In Table 6 the concentrations of methyl bromide and CO<sub>2</sub> are shown at each sampling point, 1h, 24h and 48h after application. Methyl bromide concentrations were generally much lower than at Settlers, and at some points very little gas was measured. In contrast with the Settlers result, methyl bromide concentrations tended to be lower towards the bottom of the bin. The 24-h readings were generally poorer than the 48-h readings, which indicated that it took some time for the gas to disperse through the grain. However, insect mortalities (Table 4) indicates that uniform dispersion was not reached even after 7 days, as survival occurred in some cages. The Symap printouts (Fig. 5) identify the centre of the bin as the main problem area, and to a lesser extent also the bottom. On the other hand, no survivors from the natural infestation were found in the 25-kg samples of grain that were screened after fumigation, and this suggests that some surviving insects could have gone undetected at Settlers where the numbers of naturally infesting insects were much lower than at Driefontein.

### 3.3 Bloekomspruit

At Bloekomspruit, methyl bromide concentrations (Table 7) closely resembled those at Driefontein (Table 6), except at the bottom of the silo where very high concentrations were measured. In this respect there is similarity with the Settlers results. The Symap printouts show that low concentrations occurred in the centre top half of the grain, and also in the entire lower half except for 3 m at the base, where a very high concentration was maintained for the full fumigation time. It was also evident from these figures that the concentration in the top half of the silo declined with time, while that in the lower half increased.

When the Symap printout of mortalities at Driefontein was studied, it was thought that the gas distribution might be influenced by an upsurge of relatively warm air at the centre of the bin in response to a cold, heavy layer of carbon dioxide and methyl bromide. Temperature probes were therefore used at Bloekomspruit to establish the role of gas temperatures, but the figures obtained (Table 8) do not appear to fit the gas distribution patterns in Fig. 6.

Generally, methyl bromide concentrations were high enough for a long enough time to give complete mortality of caged *T. castaneum* (Table 9), but low mortalities at the centre at 14 and 17 m below the grain surface confirm that very little methyl bromide reached these areas. Poor control was also obtained in more peripheral cages 20 m down, an area previously identified as a problem area.

## 4 CONCLUSIONS

It would seem that the results of the Israeli tests and the Settlers test are insufficient to conclusively demonstrate the successful application of this fumigation technique. Also, there appears to remain some doubt about the usefulness of CO<sub>2</sub> to act as a carrier for methyl bromide towards the bottom of the bin but this was not investigated during our tests and the probable benefits of adding CO<sub>2</sub> are not being contested.

The results of the Driefontein test and especially the Bloekomspruit test provide conclusive evidence of well-defined problem areas in the grain bulk where methyl bromide concentrations were too low to ensure complete kill. Apparently, some air was trapped below the heavy CO<sub>2</sub> and methyl bromide from where it appeared to escape in the form of huge, extremely slow-moving bubbles. Given sufficient time, and provided that the bin is sufficiently gastight to retain the gas long enough, methyl bromide may eventually disperse to these problem areas in sufficient quantities to ensure complete kill. However, more uniform dispersion can probably be attained much quicker by slow circulation with a fan.

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Editors Note: Part of the data here has been published in *Phytophylactica* (Viljoen, J.H., Coetzer, J.J. and Vermaak, C.J. (1981), 13,127-137. Fumigation trials with a mixture of methyl bromide and carbon dioxide in larger silo bins).

Table 1. Summary of bin dimensions, their contents, and rates of application of methyl bromide and carbon dioxide during this test series and those of previous authors.

	Settlers	Driefontein	Bloekomspruit	Rehovot*	Brurim*	Heilbron**
Bin height (m)	27.7	32.3	31.5	17	20	27.4
Bin diameter (m)	6.8	15.2	15.2	4.2	5.0	5.5
Bin volume (M <sup>3</sup> )	± 1000	± 5000	± 5000	240	400	± 680
CO <sub>2</sub> Dosage (g/m <sup>3</sup> )	250	115	150	250	250	-
CH <sub>3</sub> Br Dosage (g/m <sup>3</sup> )	50	50	50	50	50	64
CO <sub>2</sub> applied as	gas	snow	dry ice	dry ice	dry ice	-
Bins contents	sorghum	maize	maize	wheat	wheat	maize

\* Calderon & Carmi, 1973

\*\*Smit *et al.*, 1959



Table 2. The number of live insects in 10-kg samples of sorghum, taken at different depths from the bin at Settlers, before fumigation with a mixture of methyl bromide and carbon dioxide.

Depth below Grain Surface (m)	Species			
	<i>S. zeamais</i>	<i>S. granarius</i>	<i>T. castaneum</i>	<i>Cryptolestes sp.</i>
6.1 .....	1	-	-	-
12.2 .....	1	-	-	-
18.3 .....	32	2	-	-
(27.7m)..... (Grain outlets)	248	1	10	14

Table 3. The number of live insects in 10-kg samples of maize taken at different depths, and the temperature of the grain at those points in the bin at Driefontein, before transfer to another bin and fumigation with a mixture of methyl bromide and carbon dioxide

Depth below grain surface (m)	Species		Temperature
	<i>T. castaneum</i>	<i>Cryptolestes sp.</i>	
0 .....	272	1,304	28.5
3.0 .....	4	3	24.0
6.7 .....	7	328	25.5
10.4 .....	1	52	31.5
14.0 .....	3	165	31.0
17.7 .....	2	20	28.0
Outlet valve	2	20	22.5

Table 4. The percentage mortality in insect cages at Driefontein after fumigation with a mixture of methyl bromide and carbon dioxide. Presented here, are those cases in which a complete kill of all test species was not obtained.

Sample No.	<i>Sitophilus granarius</i>	<i>S. zeamais</i>	<i>Tribolium</i> spp.	<i>Rhyzopertha dominica</i>	<i>Onyzaephilus surinamensis</i>	- x
B3	83.3	90.6	11.9	69.8	64.0	63.9
C3	30.8	48.8	24.8	93.1	22.2	43.9
C6	33.3	50.0	81.6	88.6	20.0	54.7
D3	46.4	57.0	5.0	88.4	24.2	44.2
D4	78.1	81.3	80.7	100	96.7	87.4
D5	59.3	61.7	91.9	100	100	82.6
D7	94.6	98.0	91.9	100	100	96.9
D7	98.0	100	98.0	100	100	99.2
D9	76.9	96.2	88.1	100	97.4	91.7
E1	48.2	41.2	31.5	100	80.9	60.4
E2	52.2	55.5	57.8	100	64.3	66.0

Table 5. The pressures (cm water) that developed at different points inside the Driefontein bin, 30 and 60 min after application of CO<sub>2</sub> was begun

Sampling Point No <sup>*</sup>	30 min	60 min
Headspace .....	12.5	17.5
1 .....	9.7	19.7
2 .....	9.7	20.0
3 .....	8.0	19.7
4 .....	7.0	16.2
5 .....	9.6	20.0
6 .....	8.4	19.5
7 .....	8.4	19.5
8 .....	7.7	17.0
9 .....	9.5	20.0

\* See Fig. 2 for position of sampling points

Table 6. Gas concentrations at 9 positions in the Driefontein bin, 1 h, 24 h and 48 h after the gases were applied

Sampling point No.*	CH <sub>3</sub> Br(g/m <sup>3</sup> )			CO <sub>2</sub> (%)		
	1 h	24 h	48 h	1 h	24 h	48 h
1 .....	1.8	0.4	tr	0.3	0.6	2.3
2 .....	1.2	tr	0.2	0.7	1.1	5.9
3 .....	-	8.9	15.7	-	1.1	2.2
4 .....	-	0.9	11.8	tr	0.4	3.1
5 .....	-	0.6	2.0	0.4	2.2	4.7
6 .....	-	11.8	17.1	16.0	1.8	3.2
			13.6			3.2
7 .....	0.8	tr	0.3	0.3	3.4	5.3
8 .....	-	16.8	19.3	5.8	2.8	3.3
9 .....	-	-	21.4	10.4	-	3.0

tr = trace

\* See Fig. 1 for position of sampling points

Table 7. The concentration of methyl bromide at Bloekomspruit ( $\text{g}/\text{m}^3$ ) at different sampling points in the grain bulk and at various intervals after application of the gas at  $50 \text{ g}/\text{m}^3$

Metres down and sampling point No.	Hours after application of methyl bromide								
	0	6	14	19	26	37	62	86	110
5 1.....	44.5	28.5	10.4	7.7	4.8	4.7	4.4	3.1	2.3
2.....	8.7	8.8	12.6	12.8	9.8	8.6	6.1	3.6	2.1
3.....	0.5	0	2.6	0.2	0.2	0	0.2	0.9	1.7
4.....	82.0	25.0	13.0	16.8	13.2	8.5	7.2	5.5	4.1
5.....	25.0	2.5	2.7	2.7	2.1	1.0	2.4	2.1	1.1
11 1.....	0.8	0	0.1	0.7	0.7	0.8	1.5	1.4	0.8
2.....	50.0	30.0	16.4	18.8	11.6	7.7	7.1	5.8	5.0
3.....	1.0	0	0.1	0.2	0	0	0.1	0.5	5.6
4.....	19.2	15.2	13.8	1.2	10.8	4.8	8.8	7.2	5.7
5.....	0.2	0	0.1	1.0	0.7	0.8	2.3	2.2	1.8
17 1.....	0.2	0	0	0.9	1.3	0.7	1.4	1.9	1.7
2.....	0.3	0	0	0.7	2.3	1.4	4.2	2.4	1.9
3.....	0	0	0	0.3	0	1.1	0.6	0.4	2.0
4.....	0.2	0	0.3	1.2	0.6	1.0	3.5	3.4	3.1
5.....	0.6	24.8	17.2	13.8	10.4	3.1	6.5	4.4	3.2

Table 7 (continued)

Metres down and sampling point No.	Hours after application of methyl bromide								
	0	6	14	19	26	37	62	86	110
23 1.....	0.1	0	0.4	1.5	0.1	2.0	2.6	2.1	1.7
2.....	0.1	0.4	6.6	6.2	4.8	1.6	2.3	1.9	0.7
3.....	0.1	0	4.3	8.6	10.8	3.5	12.0	5.8	4.0
4.....	0	0	5.7	7.8	7.2	2.5	5.5	4.2	4.5
5.....	3.7	0.1	4.5	4.3	2.3	1.6	4.3	3.6	3.1
29 1.....	14.2	82.0	88.0	64.0	55.0	55.0	55.0	45.0	28.0
2.....	110.0	110.0	110.0	110.0	110.0	110.0	98.0	90.0	72.0
3.....	110.0	110.0	110.0	110.0	110.0	110.0	107.0	90.0	79.0
4.....	110.0	110.0	110.0	110.0	110.0	110.0	110.0	86.0	71.0
5.....	18.0	110.0	108.0	86.0	72.0	75.0	52.0	29.0	21.0

Table 8. The Grain temperatures ( $^{\circ}\text{C}$ ) measured at Bloekomspruit after application of the gases

Metres below Grain surface	Hours after application of methyl bromide											
	0	3	4	8	11	18	23	30	41	64	88	110
10.....	9	27	27	29	25	22	2	10	30	13	9	9
5.....	8	27	27	27	25	20	2	10	28	14	9	9
2.....	6	24	24	23	23	18	1	9	26	12	9	9
1 (north side)	5	22	24	22	24	17	10	6	14	-2	-3	-2
1 (south side)	5	20	23	21	24	16	1	9	24	11	8	6





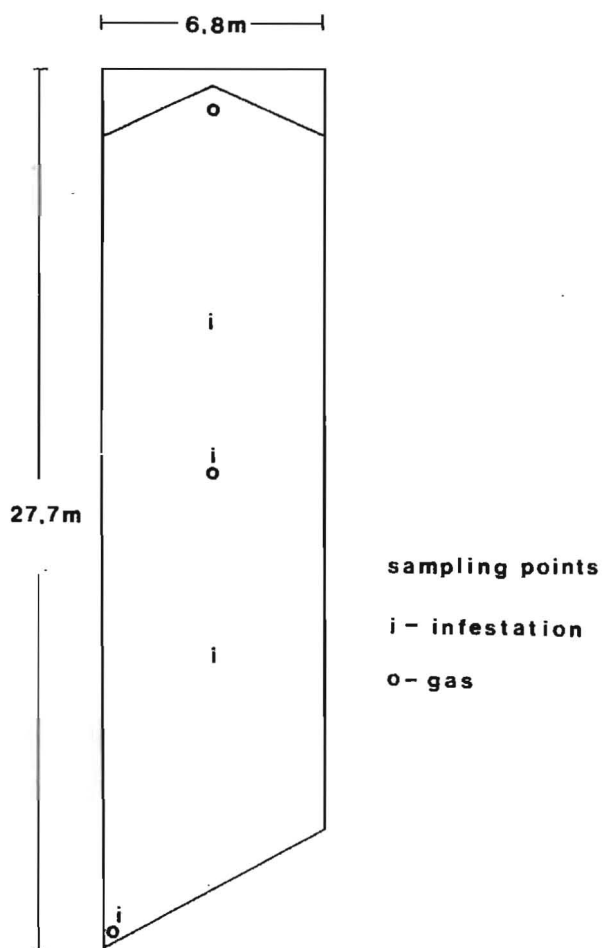


Fig. 1 The scheme of the Settlers test.

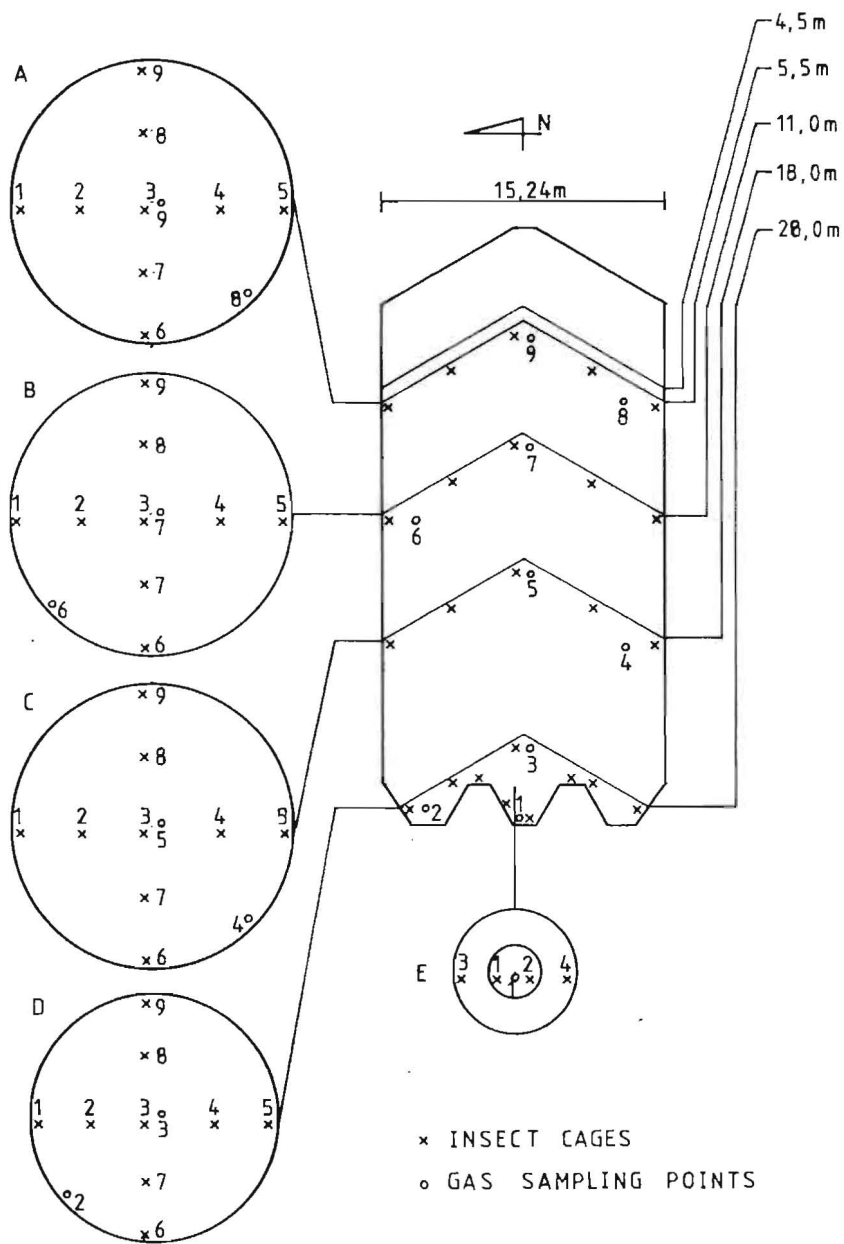


FIG. 2 THE SCHEME OF THE DRIEFONTEIN TEST.

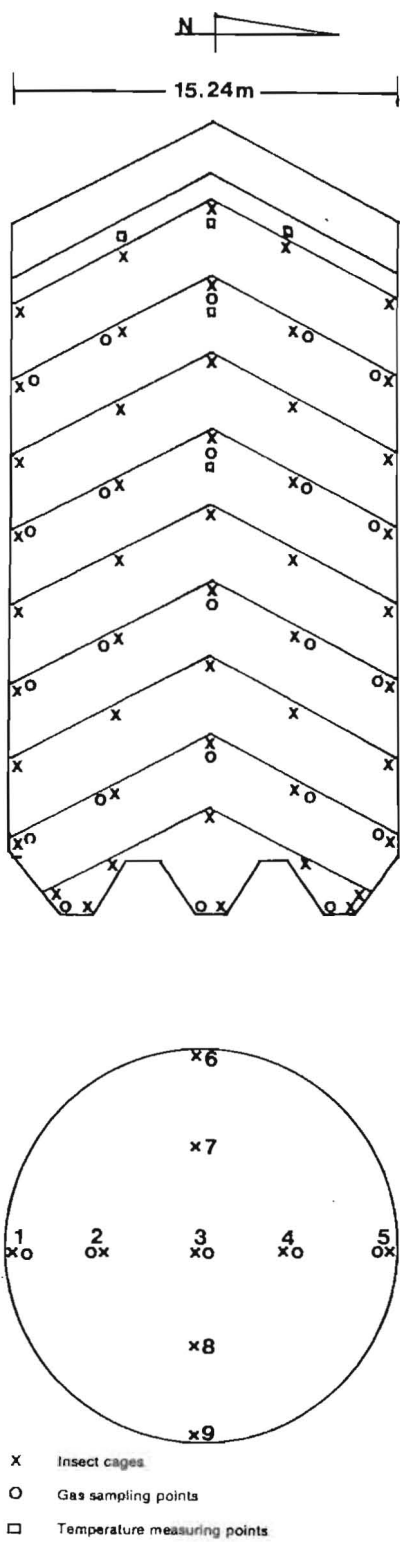


Fig. 3 The scheme of the Bloekomspruit test.

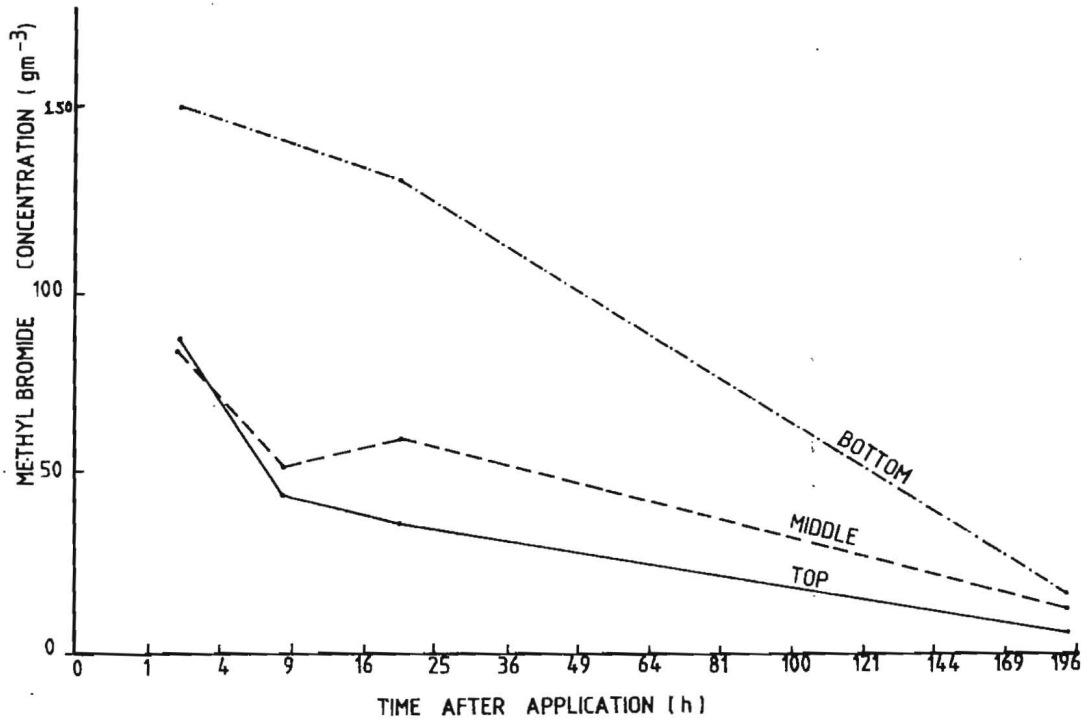


Fig. 4 The concentration of methyl bromide at the top, middle and bottom of the Settlers bin with increase in time.

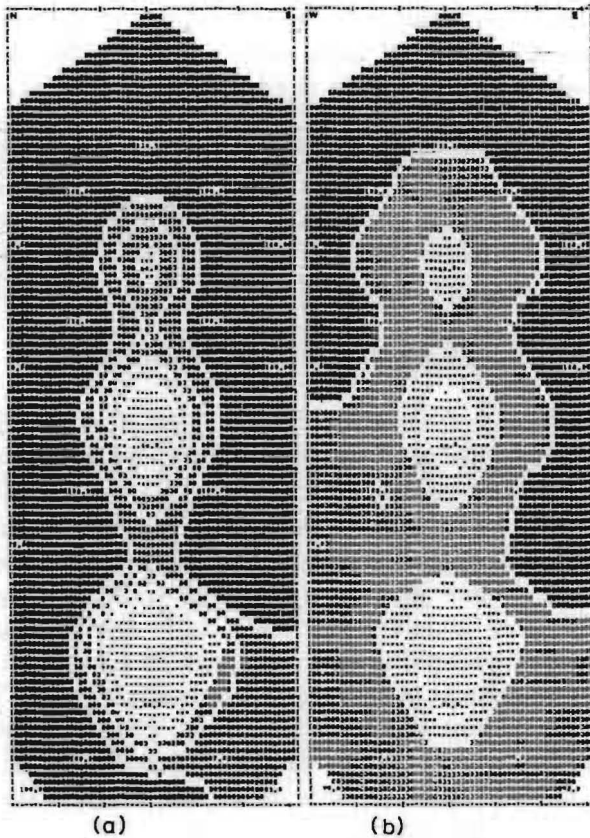


Fig. 5

The distribution of methyl bromide in the Driefontein silo as derived from insect mortalities after 7 days exposure. Darker shades represent higher concentrations (a) on the N-S plane (b) on E-W plane.



0h



6h



14h



19h



26h



37h

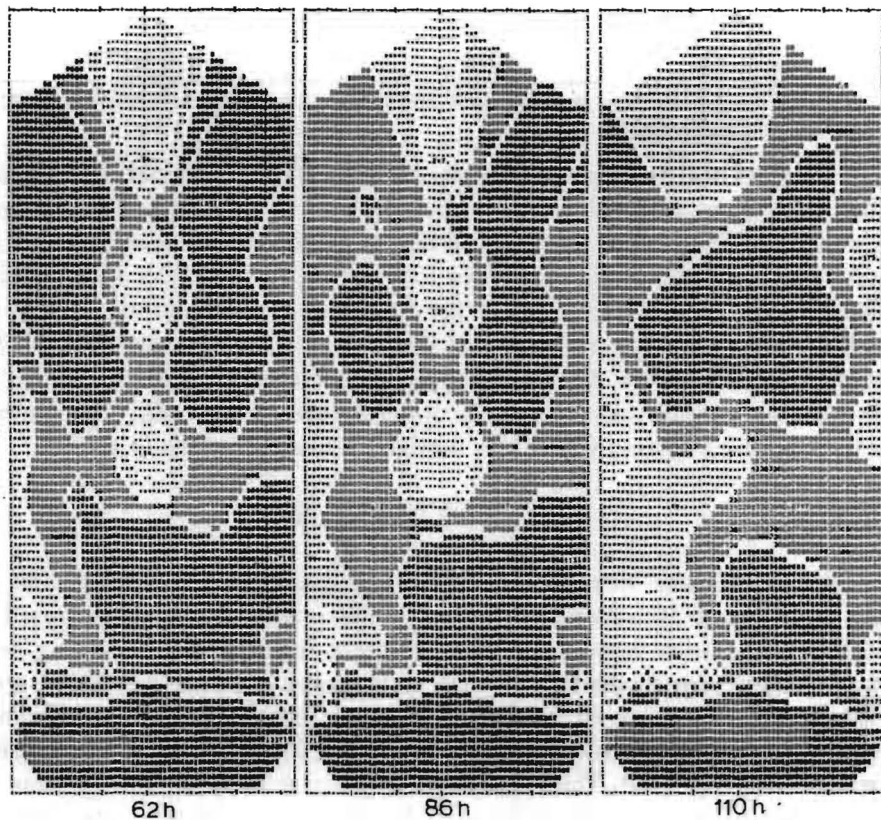


Fig. 6

The distribution of methyl bromide at intervals after application to the Bloekomspruit silo.