# Methallyl chloride as a fumigant against insects infesting stored products

# METHALLYL CHLORIDE AS A FUMIGANT AGAINST INSECTS INFESTING STORED PRODUCTS

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ACADEMISCH PROEFSCHRIFT TER VERKRIJGING VAN DEN GRAAD VAN DOCTOR IN DE WIS- EN NATUURKUNDE AAN DE RIJKSUNIVERSITEIT TE UTRECHT, OP GEZAG VAN DEN RECTOR MAGNIFICUS DR TH. M. VAN LEEUWEN, HOOGLEERAAR IN DE FACULTEIT DER GENEESKUNDE, VOLGENS BESLUIT VAN DEN SENAAT DER UNIVERSITEIT IN HET OPENBAAR TE VERDEDIGEN OP MAANDAG 5 JUNI 1939, DES NAMIDDAGS TE 3 UUR

DOOR

CORNELIS JAN BRIEJER
GEBOREN TE LEIDEN

1939
MEIJER'S BOEK- EN HANDELSDRUKKERIJ
WORMERVEER

*Aan mijn Vrouw*

*Aan mijn zonen Paul en Martijn*

Dit proefschrift werd goedgekeurd door den promotor: PROF. DR. L. P. DE BUSSY.

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Bij de genomen proeven werd in ruime mate medewerking verleend door Mejuffrouw G. F. E. M. DIERICK en de Heeren F. E. LOOSJES en PH. GEROLT.

Hiervoor mijn hartelijken dank!

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## GENERAL INTRODUCTION

For those who are interested in the control of noxious insects but have only very little or no knowledge of entomology a *general introduction* is given, which probably contains very little news for entomologists.

An insect is primarily caused by natural equilibrium being disturbed, as a result of which the conditions for insect life become disproportionately favourable. In many cases the equilibrium is disturbed by man who lays out plantations, stores goods and carries insects to areas where they did not exist previously.

By improving agricultural and horticultural plants, varieties are obtained which are even more susceptible to insect attack. By crowding a small area with plants conditions are made more favourable for insects.

Insects are very often carried from one area to another where the conditions are more favourable, the more so, if, as is very often the case, the enemies of these insects do not occur in the new area.

Large quantities of goods are accumulated only by man. Very often the storage conditions of the goods are very auspicious to the development of an insect fauna.

The aim of control of insect pests should be in the first place to restore the disturbed equilibrium, hence to make the conditions which have become too favourable, unfavourable again. The *cause* of the insect pest is then removed; so this method of control may be called a *causal* one. If this method is applied the pest should first be *analysed*. A close study must be made in every case of the direct causes of the pest. Sometimes it will be possible to eliminate these. If, for instance, a variety of insects has been carried from one area to another, but its enemies have not been brought along with it, they may be introduced later, thus eliminating the cause of the pest. However, the cure is not always as simple and straight-forward as this. It is possible that the insect itself thrives in the new area, but that its enemy cannot live there. The case then becomes a little more complicated and one way to meet the difficulty would be to find a new enemy that can live in this area.

In many cases there are even more complications. Methods for growing must be changed so that they will not longer suit the life circle of the insects; varieties of plants with a high resistance should be grown, and so on. Generally, these methods consist in either adding a factor or withdrawing one from the conditions for life of the insect, as a result of which these conditions become unfavourable. This may be called *natural* or *biological* control, and may be considered as work belonging to the field of biology. This control method is characterized by the fact that the effect is permanent, since the pest will generally not return as a result of the same cause.

In many cases it is not possible, however, to affect the conditions for life of the insect by natural means. In that case means should be found to kill the insects and to limit the pest as much as possible, though not removing the cause of the trouble. It must be remembered, however, that there remains a chance of the pest returning.

This kind of control will often be effected with the aid of chemicals. This may therefore be referred to as *chemical* or *technical* control. It should also be preceded by accurate biological analysis. For the actual control, however, the biologist will need the help of the chemist and the physicist and generally also of the technician.

In agriculture and horticulture biological control will in many cases afford relief. This is not the case with insect pests in stored goods. Storing of goods is unavoidable and only in very few cases can the method of storage be changed. Here the conditions created by man are the cause of the trouble. Methods such as those worked out by Rank (1), in which a continuous current of air is passed through the goods, would in the long run be too expensive and can not be applied in the case of many products, such as tobacco. In by far the most cases chemicals must therefore be used.

The *extent* of this kind of pests is still too little known. Just as the presence of bed-bugs in houses is kept secret by the occupants, the owner of warehouses endeavours to hide the fact that insect pests occur in them. The owners of the goods would object — and rightly — and in some cases might even claim damages. On the other hand the consumers would be greatly displeased to know that their food is, or has been, infested with „vermin". For these reasons the control of the pest is often carried out in secrecy. Yet the pest *is* controlled although by no means in a sufficient degree. As a result of this many warehouses still swarm with millions of moths and as many weevils as well as larvae of both.

It is the task of the biologist to find and to try out the means of putting an end to these pests in the simplest and cheapest manner.

# CHAPTER I

## INSECTS USED AND KNOWN MEANS OF CONTROL

*Particulars concerning the insects used during this investigation and concerning the fumigants which are already known for controlling them*

The investigation described below is meant to be a contribution towards the control of insects in stored goods with the aid of a gas poisonous to these insects. It was carried out mainly on species of Calandra occurring in stored grain. The gas may also be used, however, for the control of other kinds of insects in other products. These applications are also mentioned in my investigations. In all cases, however, Calandra granaria L. were used for the experiments.

### I. INSECTS USED

*Breeding method.*

The test object I mainly used was Calandra granaria L. and Calandra oryzae L. from my own, well-kept, cultures. During the summer the insects were bred at room temperature (18—22° C) and during the winter part of them in an incubator at 20° C and the rest in an incubator at 27—28° C. The latter part was kept at 20° C for at least two or three days before fumigation. When adults were used, young, strong specimens about four weeks old were taken.

The maintenance of the cultures offers few difficulties. It is important that the degree of humidity should be sufficiently high, since otherwise the weevils will not lay any eggs.

According to Schulze (2) Calandra granaria does not oviposit at a relative humidity below 30—40 %. Moreover, the lifetime of the adults is shortened if the humidity is too low.

I am able to confirm the fact that neither of the Calandra species multiplies in a very dry atmosphere. C. oryzae is not so sensitive as C. granaria in this respect. I observed several cultures of Calandra on wheat containing both species. As these cultures were kept a little too dry C. granaria died off altogether while C. oryzae thrived.

*Systematic position.*

There is no difference in opinion as regards the systematic position of Calandra granaria L. and Calandra oryzae L. In American literature, however, these insects are generally mentioned by the names Sitophilus granarius L. and Sitophilus oryzae L. Sometimes in literature a certain species, referred to as Calandra zeamais Motsch., may be encountered. Opinions differ however, as to whether this is a separate species or a larger variety of C. oryzae. I found large-sized Calandra in a batch of maize which were all determined as C. oryzae. I bred normal-sized C. oryzae obtained from rice for several generations on maize and observed a considerable increase in size. According to Cotton and Good (3), C. oryzae and C. zeamais are identical. Zacher (4), Weidner (5) and Andersen (6), on the other hand, consider these insects to be different species.

*Anatomy and biology.*

An excellent description of the anatomy and biology of C. granaria is given by Müller (7). The information given there also applies to C. oryzae.

The publication by Teichmann and Andres (8) is somewhat older and contains beautiful, coloured illustrations.

A very good monograph was recently published by Andersen (6). The following facts are important for the control of these insects. The entire development of the Calandra takes place inside the grain of corn. The full-grown weevil bores a hole in a grain of corn with its mandibles and the egg is deposited in it. According to Zacher and Andersen the opening is closed by means of a secreted substance. Müller, however, is of the opinion that although a glass-like, transparent lump is attached to the egg, the opening is not entirely blocked by it. The fact that the eggs are within easy reach of fumigants pleads for Müller's opinion. It is generally agreed that only one larva can develop in one grain. Although Zacher states that more than one egg is deposited in one grain, Müller maintains that these originate from different females and that only one larva develops completely. Only in maize it should be possible that more than one larva may develop in one grain. Normally, larvae and pupae remain in the grain during the whole of their existence. It is impossible therefore to tell from the appearance of a batch of grain whether it is infested. This can only be stated with certainty by opening a great number of grains or by placing a sample of the shipment in an incubator at about 28° C for six weeks. If during that period no weevils appear the shipment may be considered to be not infested.

The duration of the total development from egg to adult is very much dependent on the prevailing temperature. For Germany in the summer Zacher gives a period of roughly two months. In my cultures at 27—28° C the duration of the development amounted to about six weeks.

Opinions differ as regards the number of progeny of one female Calandra. According to Andersen this number is about 160. According to my own observations this number depends very much on the humidity of the wheat. At a relatively high humidity the number will certainly be much higher than 160 and will probably amount to many hundreds.

In a seriously infested lot of grain or in an overcrowded culture it may occur that older larvae which during their first stages have lived inside parts of a grain of corn later on may be observed to lie exposed. They can then develop normally in the flour formed by the infestation. Eggs and young larvae cannot develop outside the grain of corn.

According to Zacher C. granaria may develop in wheat, rye, maize, barley, malt, rice, millet, buckwheat, sweet chestnuts, acorns, maccaroni and noodles, while C. oryzae can also develop in cotton seed.

C. granaria is an insect which only occurs in stored goods and cannot fly. C. oryzae can fly, however, and therefore would be able to leave the sheds and infest the crops in the fields.

Schulze (2) states that C. oryzae makes very little use of its wings. I often observed that weevils which had been killed by fumigants lie with their wings and elytra spread, while I sometimes noticed them flying around in the rooms where they were being bred.

Both Calandra species are negatively phototropic.

*Damage.*

Statements on the damage which may be caused by Calandra vary greatly. In any case the damage is considerable. It does not only include the grain which has been devoured, but the presence of many Calandra increases the humidity of the grain, as a result of which overheating may occur. Furthermore, the germinating power of seed-corn is considerably impaired.

In order to obtain an idea of the damage caused by the grain being devoured, I put 1000 adults of C. granaria into 4 kg of wheat in the incubator at 27—28° C. After a period of seven weeks the wheat was reduced to 3.67 kg which means a decrease of 8.25 % and the number of weevils had risen to many tens of thousands.

## II. KNOWN MEANS OF CONTROL

Corn weevils have always been very difficult to control, one of the reasons for this being that the larvae and pupae pass their life-cycle concealed in the grain. One of the oldest methods for control is to submit the grain to repeated motion. The weevils are disturbed and emerge from the grain. This may be demonstrated in the laboratory by shaking a culture of Calandra. This method, however, has no effect on the younger stages.

A primitive repellent is fresh hay or straw. In Holland I noticed some farms in the province of Groningen where this method is still applied. According to Zacher the active constituent is coumarine. In such a small dose, however, it has no appreciable effect.

A more modern method is coating the walls of the storerooms with chemicals, e.g. aniline. Vide Zacher (9).

From the bionomy of the insects described above it is clear that these and similar methods cannot ensure efficient control. I should like to define efficient control as: "one operation or one series of operations by which all insects present in all stages of development are killed". The effect should be such that the insects cannot occur again in rooms or goods which have been treated, unless they are introduced from some other place.

Since species of Calandra and the majority of insects occurring in other products are spread throughout these materials only those means of control can be effectively applied in which the substance used penetrates all through the products. As such may be considered temporary increase or decrease of temperature. This method can, however, only be applied in exceptional cases, while furthermore the cost is too high.

Further, *fumigation* comes into consideration. This method consists in the introduction of a quantity of gas poisonous to the insects into a properly closed storeroom containing the products. After a certain period the gas is removed by means of ventilation. A list of the gases which are generally used for this purpose is given by Frickhinger (10). A great deal of information may also be found in circulars No. 369 and 1313 of the U.S. Department of Agriculture (11). I will briefly mention here those fumigants which in actual practice are applied in considerable quantities, though this list does not pretend to be exhaustive. All these products are used both for the control of Calandra species and other insects in stored goods.

*Carbon disulphide*, $CS_2$.

This is one of the oldest fumigants. It is mainly used as a soil insecticide. Vide Trappmann (12). He advises 200—300 g per cub. m for fumigating stocks of grain (not seed-corn) for 32 hours. This material was further used for the control of Lasioderma in tobacco, as was communicated by De Bussy (13).

One of the greatest drawbacks to the use of carbon disulphide is its inflammability. Hinds (14), for instance, states: "it is hardly safe to have steampipes very hot or to turn on or off an electric light or fan. Even the heavy striking of a nail with a hammer might cause an explosion".

Scherpe (15) also draws attention to the high inflammability of $CS_2$. In some countries fire insurance is said to be suspended during fumigation, while in U.S.A. the fumigation of railway carriages with $CS_2$ is prohibited. Scherpe also describes difficulties owing to the grain absorbing the gas too strongly.

*Hydrogen cyanide*, HCN.

The control of Calandra by means of hydrogen cyanide is described by Teichmann and Andres. They state that Calandra granaria is highly resistant to HCN. For efficient control about 3 % by vol. is necessary, corresponding to 30 g of HCN per cub. m.

Another great disadvantage of this gas is its extreme toxicity to human beings. In many countries there are legal measures restricting the use of this fumigant. See, inter alia, Lentz und Gassner (16). These measures, however, have not been able to prevent fatal accidents. For reference see, inter alia, Frickhinger.

*Chloropicrin*, $CCl_3NO_2$.

After the great war the idea arose that war gases might also be used for constructive purposes. These gases were too poisonous to human beings, however. Only chloropicrin can be used as a fumigant against insects. Experiments with this gas against Calandra granaria are described by Wille (17) among others. A complete bibliography of chloropicrin is given by the U.S. Department of Agriculture (18).

Its disadvantages are that it badly irritates the eyes, nose, throat and all other respiratory organs and that it adversely affects the germinating power of the seeds. As a dosage for actual practice Wille advises 40 ml per cub. m for 24 hours.

*Hydrogen phosphide*, $PH_3$.

This gas is also used against Calandra in various ways. Flury (19), however, states that inhaling this gas by man may cause death within two or three days. This is sufficient reason to bar its use as a fumigant.

*Areginal.*

The composition of this material is not known with certainty. Probably it consists of a mixture of ethyl- and methyl formate. The insecticidal effect of this gas is roughly equal to that of carbon disulphide, while its mixtures with air are said not to be explosive. Frickhinger states that areginal is not dangerous to man, which, however, is contradicted by the results of my experiments on mice. Frickhinger also states that areginal does not affect the germinating power of seeds.

Kleine (20), however, concludes from his experiments that areginal is highly inflammable and should be handled with the utmost care, and besides that it strongly affects the germinating power of seeds.

*Ethene oxide*, $C_2H_4O$.

This material was first described as an insecticide by Cotton and Roark (21) in 1928. In the subsequent ten years an extensive literature arose of which a good summary was made by Frickhinger.

Pure ethene oxide is highly inflammable and very easily gives rise to explosions. Cf. Lentz and Gassner. In order to minimize this danger of explosion it is mixed in various proportions with carbon dioxide, which according to the investigations of Hazelhoff (22) also stimulates the respiratory centres of the insects.

Besides its great inflammability ethene oxide has the drawback that it strongly affects the germinating power of seeds and that it is very poisonous to man. Investigations in this field were carried out by Flury (39) who came to the conclusion that especially the after effect of ethene oxide is very dangerous to the human organism. The symptoms of poisoning occur quite a long time after the gas has been inhaled, so that it may by that time be too late to afford assistance.

Owing to its low boiling point this material and its mixtures can only be stored and transported in steel cylinders, which increases the cost of the fumigation considerably.

*Methyl bromide*, $CH_3Br$.

This material was first used as an insecticide in California in 1935. Its activity is described in recent publications by Mackie and by Fisk and Shepard (23). According to these publications methyl bromide has attractive properties as an insecticide. A great disadvantage was pointed out by Lepigre (33), viz. too great a quantity of HBr remains behind in the fumigated foodstuffs, which might endanger the health of the consumers.

## CHAPTER II

# GENERAL LABORATORY INVESTIGATIONS WITH METHALLYL CHLORIDE

Apart from their favourable properties, the fumigants which are in use at present have still so many disadvantages that efforts should be made to invent other materials which either do not have these disadvantages at all or only to a smaller extent. It is of the greatest importance to find a material which is about just as toxic to insects as the fumigants already known, but which is less toxic to man.

For this reason I carried out investigations with *methallyl chloride*. This material had only been described as an insecticide in the patent literature (24). I published a short paper on the investigations in Nature (25), while further information was communicated by me at the 7th International Congress for Entomology at Berlin (26).

Methylallyl chloride or methallyl chloride, which will further be referred to as M, is a colourless liquid which has the following structural formula:

$$\begin{array}{l} CH_2 : \underset{\displaystyle CH_3}{\underset{|}{C}} \cdot CH_2Cl \end{array}$$

The specific gravity at 20° C is 0.925 and the boiling point 72° C. The liquid itself is inflammable. The explosion range of mixtures of M vapour with air lies between 93 gr/cub. m and 375 gr/cub.m.

The liquid evaporates readily in the open air, its latent heat of evaporation at 20° C is 89 cal./kg.

The odour of the liquid is strong, but not unpleasant.

While investigating this fumigant I endeavoured to answer the following questions:

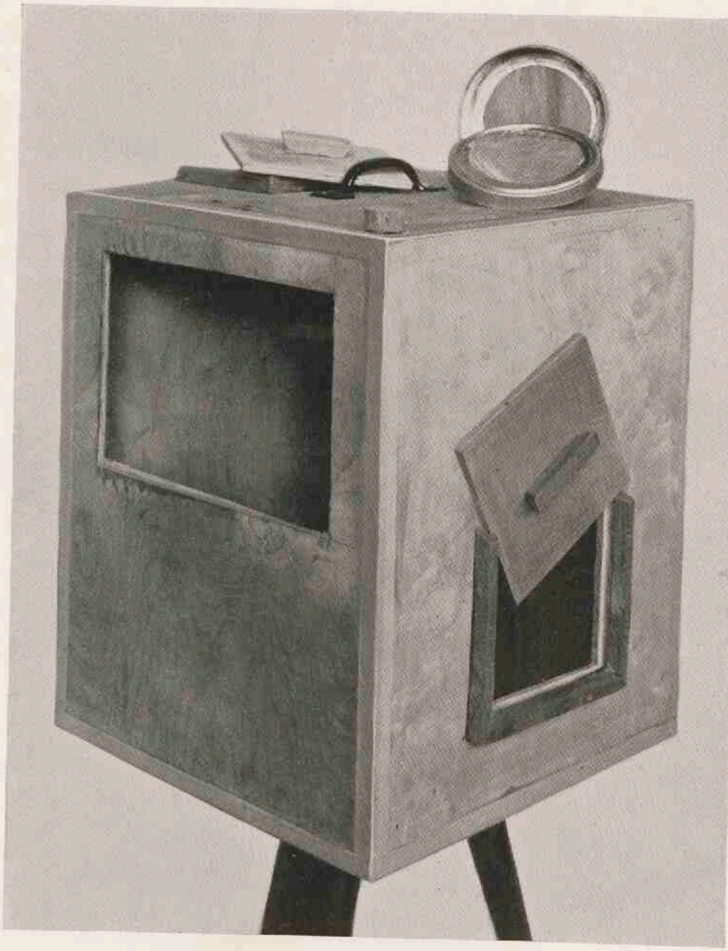
1. What should be the dose to kill insects in an empty space?
2. In what manner does the fumigant spread in an empty space?
3. What is the penetrating power of the gas into the goods which are to be fumigated?
4. What influence has the presence of the goods which are to be fumigated on the concentration required?
5. What influence has the gas on the goods to be fumigated?
6. How does the gas act in actual practice?
7. What is the proportion of the concentration required to the time of exposure?
8. What substances may be added to the liquid to make the mixture non-inflammable without adversely affecting its toxicity?
9. To what extent is the gas toxic to mammals?

These questions were in the first place applied to Calandra species in stocks of grain, but the results obtained were also tested upon other insects and other products.

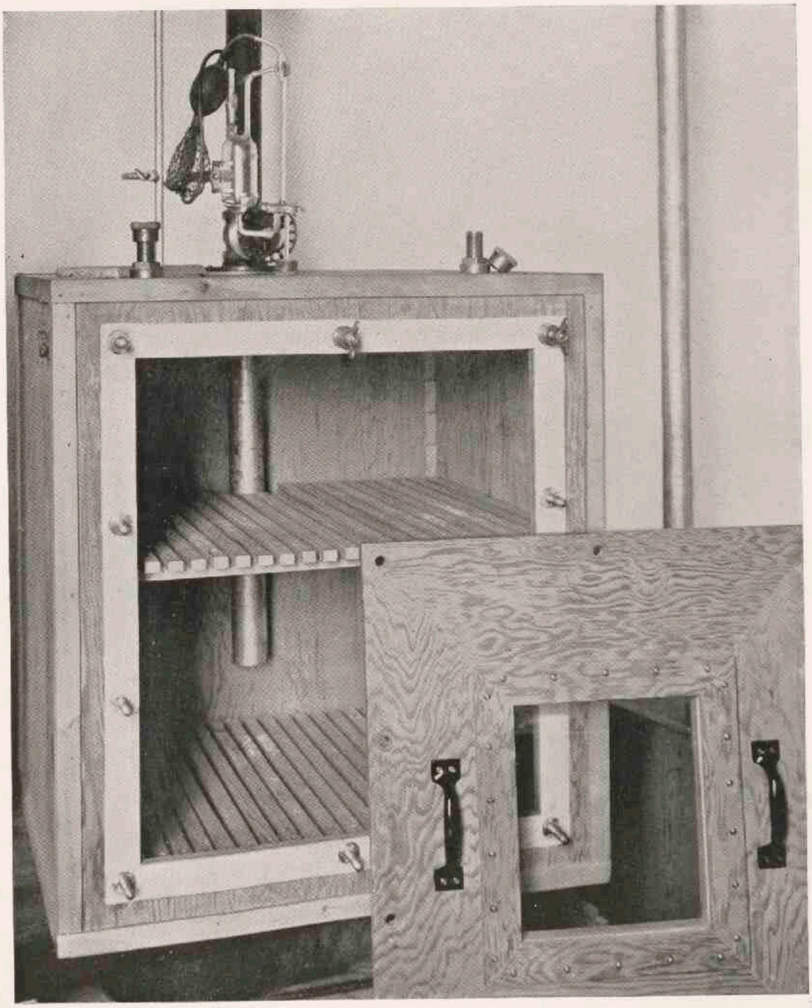
## I. DETERMINATION OF THE DOSE TO KILL INSECTS IN AN EMPTY SPACE

In these experiments I used closed wooden gassing boxes made of three-ply wood 0.8 cm thick. The dimensions are: height 50 cm, length and breadth 40 cm, while the capacity is 80 litres. The boxes are provided with two sliding panels, one on the top and one in the front. A glass window is provided at one of the sides. The insects were put in tins, 5 ½ cm high and 14 cm in diameter. The bottom and the lid are provided with gauze. Vide photograph No. 1.

In all cases some wheat was added for the insects to feed upon. The tins were placed in the gassing box on small legs



1. 80 litres gassing box with gauze tin upon it



2. 345 litres gassing box

about 2 cm high. The two sliding panels were secured by strips of surgical plaster pasted round them before each fumigation. The liquid which was to be evaporated was introduced through an opening in the top of the box by means of a 5 ml pipette graduated to 0.05 ml. Under this opening a glass disk was placed with filter paper in it. The opening was closed by means of a cork which was sealed with cellon lacquer.

The boxes were placed in a room facing North, where the temperature was 18° C and fairly constant.

The tins with the insects were taken out of the boxes 24 hours after the liquid had been introduced. The two sliding panels were opened and the boxes were degassed in a fume-cupboard, to which a powerful exhauster had been connected.

This system was worked out by P. Korringa, who, before me, carried out a number of preliminary experiments with methallyl chloride, the results of which were not published. I examined the insects in some cases immediately after they had been taken out (dir.), and in all cases 24 hours and one week after they had been taken out (24 h., 1 w.).

50 insects were used for each fumigation. In cases where this number was deviated from, this is mentioned.

*Examination of the gassed insects.*

Opinions differ about the manner of evaluating the results obtained in experiments for insect control. Not all insects are killed immediately, some of them are definitely affected, but still move their legs or antennae. The question is whether these insects should be mentioned in the results as "affected", "half dead" or otherwise. Sometimes two "half dead" insects are computed as "one dead" and "one alive", but I wish to emphasize my absolute disapproval of this procedure.

The object of the fumigation is *to kill* the insects. An insect is either dead or alive. If it is merely affected it can either recover or succumb. This can only be ascertained by keeping the animals for a certain period and examining them from time to time.

I evaluated the results as follows: the insects which in any way were still moving were considered to be alive. Only those insects which showed no movement whatever were considered to be dead. Applying this procedure the difficulty remains, however, that Calandra can simulate death for quite a long time. To the trained investigator, however, the position of the legs and antennae easily reveals whether the insect is really dead or is only simulating death. Besides, all the motionless insects were closely examined, by means of a heated glass rod. This should be done with great care so that the insects which may possibly be still alive are not burnt. In this manner the insects were sometimes checked immediately after gassing and invariably 24 hours and one week after gassing. The latter is essential since it is possible that:

*a.* the insects appear to be dead immediately after gassing, and remain motionless for a few days, but recover again afterwards;

*b.* the insects immediately after treatment appear to be affected only very slightly, but succumb in a few days.

*Procedure of the experiments and recording of the results obtained.*

During the first series of my experiments in the gassing boxes described above the duration of the fumigation and the temperature were kept constant. No special measures were taken to keep the relative humidity constant. This is usually fairly high in the Dutch climate. With these constant or nearly constant factors the dosage of gas applied was varied.

A similar method was also followed by Strand (27). Strand introduced about 30 Tribolium confusum Duv. into an Erlenmeyer flask with a capacity of 6.4 litres and observed the kill for various fumigants with increasing doses.

The results are laid down in graphs in which the percentage of killed insects are plotted on the ordinate and the concentrations of the fumigants in mg per litre on the abscissa. With the aid of the points thus obtained he draws curves which always have a sigmoid shape.

To have a criterion for comparing different fumigants this author wishes to introduce the "median lethal dose". This suggestion was based on his observation that in repeated series of experiments the results fitted best at the point of 50 % kill. For this reason he wishes to determine the dosage required to kill 50 % of the test objects. Following Trevan (28) he calls this the median lethal dose and the rate of this dose is supposed to give the relative value of the fumigant.

I wish to discuss Strand's experiments here because both his sigmoid curves and his suggestion of a "median lethal dose" have been adopted by many authors, while I do not agree with this.

I must raise the following objections against the experiments of Strand. He speaks of concentration while really he is only informed about the dose. These two conceptions are not kept sufficiently distinct by him and many others.

Concentration may be expressed as the number of mg of gas which are really present in a litre of gas-air mixture.

Dose may be expressed as the number of mg of gas which are applied per litre of space.

The concentration should be determined by taking a sample from the space filled with gas and analysing this.

The dose is always known. It is incorrect and also confusing to speak of a "theoretical concentration".

The concentration of the gas will never be the same all over the space containing the gas, unless the gas mixture is continually kept in motion, which is not done by Strand. He compares HCN and $CS_2$, a very light and a very heavy gas, while during the experiments the insects were kept at the same level in the space.

I wish to observe the following with respect to the recording of the results in sigmoid curves. In recording the results of an investigation only those data should be reported, which have really been observed as well as the conditions under which the observations were made. *Facts* therefore. Strand and others find a number of — sometimes very few — figures. These figures are plotted in a graph. There is nothing against that. But then they construct a curve along the few points obtained, which in my opinion is insufficiently justified. I admit that such a curve *may* be obtained with a very great number of test insects under ideal, standardized conditions. In most of the experiments with insects the conditions cannot be controlled so easily and the number of insects is not so great as to justify constructing such a curve with the values obtained. Evidently the reasoning is as follows: it is known that under ideal but practically unattainable conditions a curve of a certain shape *may* be obtained. A few points *are* obtained which only very roughly give the course of the curve. Then the presumed curve is drawn, which, however, in most cases does not even intersect the points found in the experiment.

In my opinion it is more correct to record only that which has *really* been observed. So a graph is obtained which is based on *facts* and not on ideal conditions which were never attained.

Like Shepard and his collaborators (29) and Peters (30) I reject Strand's suggestion to judge different fumigants with respect to each other with the aid of the "median lethal dose". The two authors mentioned, like myself, are of the opinion that fumigants which must serve in actual practice to kill *all* the insects, may only be evaluated in the laboratory by the dose which effects a kill of 100 %.

In this connection the following may be pointed out:

Strand and many others forget that insects are living creatures which must be regarded from a biological point of view. In each experiment he fumigated 30 Tribolium. These insects form a population amongst which are insects with a low, medium or high resistance to the gas. If 50 % of them are killed by an insecticide, these consist of all the weak ones and half of those with a medium resistance to the gas. If this were to be expressed in "life units", it might mean a kill of some 30 % with the median lethal dose. Besides, it is not impossible that all the male insects would be killed and the — generally fertilized — females would survive.

It should be demanded of an insecticide that, at least under ideal laboratory conditions, it kills *all* the insects, including the strongest. If the latter survive, the treatment has an opposite effect, viz. a selection takes place as a result of the survival of the fittest, a danger which always exists in the control of insects and to which too little attention has been paid up to now.

For this reason I reject both the recording of the results in sigmoid curves and comparison by means of the "median lethal dose". Instead of this I give graphs representing exclusively the facts that have been observed and a comparison by determination of the dosage at which a kill of 100 % is obtained.

In my graphs the doses applied have been plotted horizontally. On this line vertical columns have been drawn representing the corresponding kill for each dose. Side by side are given the series of observations directly after gassing (dir.), 24 hours later (24 h.) and one week later (1 w.). In this manner three series of columns were obtained, which only represent what has really been observed and yet give an excellent idea of the effectiveness of the gas in question.

## EXPERIMENTS

with methallylchloride in gassing boxes with a capacity of 80 l.
Fumigation time 24 hours

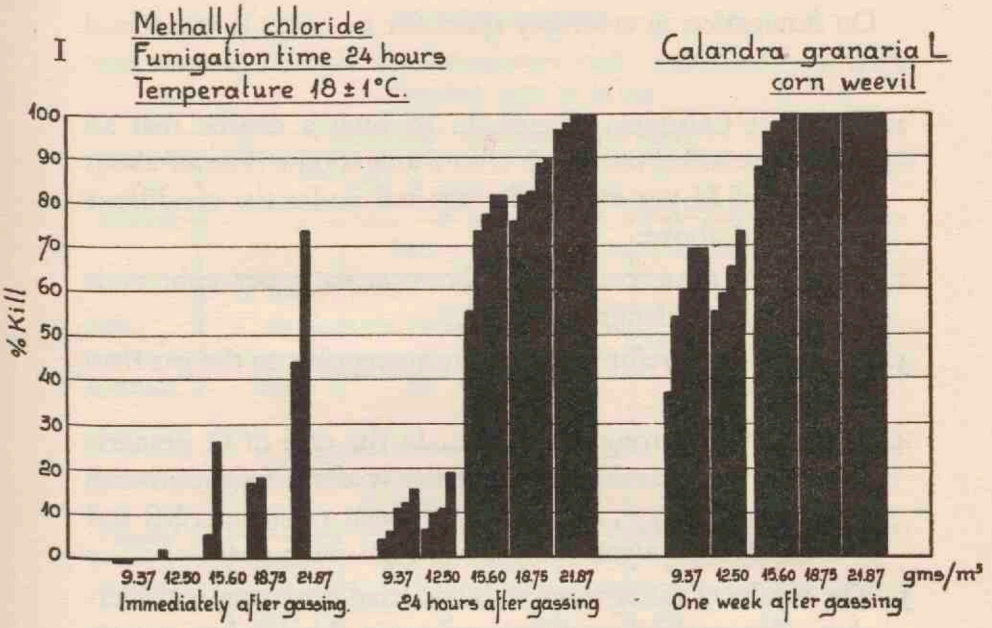
CALANDRA GRANARIA L. (Adult).

| Counted | Dose in grams per cub. m. | | | | | | Temperature |
|---|---|---|---|---|---|---|---|
| | 6.25 | 9.37 | 12.50 | 15.60 | 18.75 | 21.87 | |
| Dir. | — | 0 % | — | 5 % | 17 % | 73 % | ca. 19° C |
| 24 h. | — | 15 | — | 81 | 81 | 100 | |
| 1 w. | — | 69 | — | 100 | 100 | 100 | |

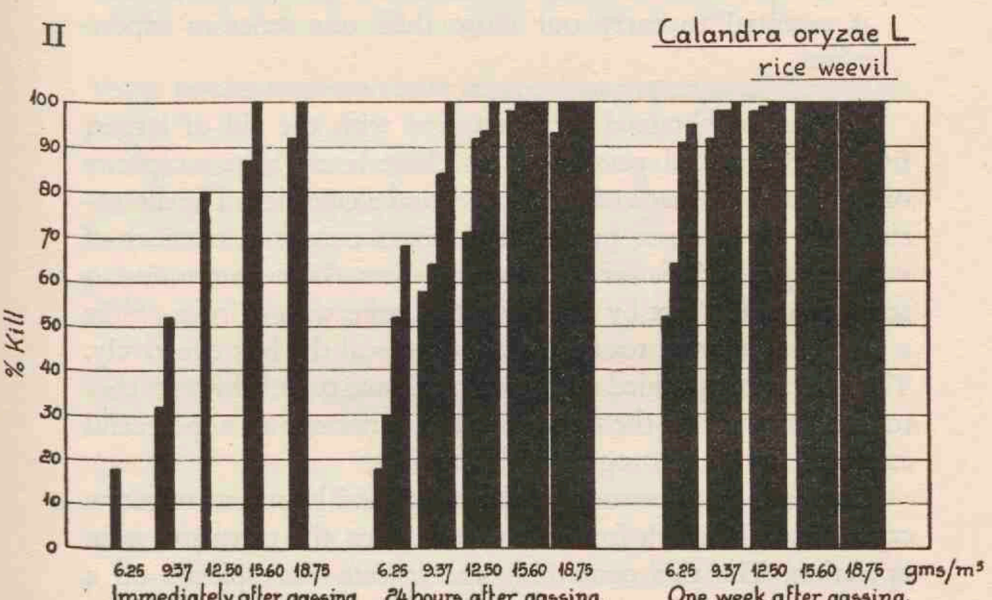
| Counted | Dose in grams per cub. m. | | | | | | Temperature |
|---|---|---|---|---|---|---|---|
| | 6.25 | 9.37 | 12.50 | 15.60 | 18.75 | 21.87 | |
| Dir. | — | 0 | — | — | 18 | — | ca. 18° C |
| 24 h. | — | 11 | — | — | 90 | — | |
| 1 w. | — | 69 | — | — | 100 | — | |
| Dir. | — | — | 2 | 26 | — | — | ca. 17° C |
| 24 h. | — | — | 10 | 55 | — | — | |
| 1 w. | — | — | 55 | 88 | — | — | |
| 24 h. | — | 6 | 11 | 77 | 82 | 96 | ca. 17° C |
| 1 w. | — | 54 | 73 | 100 | 100 | 100 | |
| 24 h. | — | 12 | 19 | 73 | 89 | 100 | ca. 19° C |
| 1 w. | — | 37 | 59 | 96 | 100 | 100 | |
| 24 h. | — | 4 | 6 | 81 | 76 | 98 | ca. 17° C |
| 1 w. | — | 60 | 65 | 98 | 100 | 100 | |
| DITTO. CALANDRA ORYZAE L. (Adult). | | | | | | | |
| Dir. | 18 | 32 | — | 87 | 92 | — | ca. 19° C |
| 24 h. | 68 | 64 | — | 100 | 100 | — | |
| 1 w. | 95 | 98 | — | 100 | 100 | — | |
| Dir. | — | 52 | — | — | 100 | — | ca. 18° C |
| 24 h. | — | 100 | — | — | 100 | — | |
| 1 w. | — | 100 | — | — | 100 | — | |
| Dir. | — | — | 80 | 100 | — | — | ca. 17° C |
| 24 h. | — | — | 100 | 100 | — | — | |
| 1 w. | — | — | 100 | 100 | — | — | |
| 24 h. | 18 | 58 | 71 | 100 | 100 | — | ca. 17° C |
| 1 w. | 64 | 92 | 99 | 100 | 100 | — | |
| 24 h. | 30 | 84 | 94 | 100 | 100 | — | ca. 19° C |
| 1 w. | 52 | 98 | 98 | 100 | 100 | — | |
| 24 h. | 52 | — | 92 | 98 | 92 | — | ca. 17° C |
| 1 w. | 91 | — | 100 | 100 | 100 | — | |

Cf. graphs I and II

I


Methallyl chloride
Fumigation time 24 hours
Temperature 18 ± 1°C.
Calandra granaria L
corn weevil
% Kill
100
90
80
70
60
50
40
30
20
10
0
9.37 12.50 15.60 18.75 21.87
Immediately after gassing.
9.37 12.50 15.60 18.75 21.87
24 hours after gassing
9.37 12.50 15.60 18.75 21.87 gms/m³
One week after gassing

II


Calandra oryzae L
rice weevil
% Kill
100
90
80
70
60
50
40
30
20
10
0
6.25 9.37 12.50 15.60 18.75
Immediately after gassing
6.25 9.37 12.50 15.60 18.75
24 hours after gassing.
6.25 9.37 12.50 15.60 18.75 gms/m³
One week after gassing.

On fumigation in an empty space for 24 hours it was found that:

1. To affect Calandra granaria L. to such a degree that all insects are killed one week after fumigation a dose of about 18.75 g of M per cub. m is required under the conditions mentioned above.
2. Under the same conditions about 12.50 g per cub. m is required for Calandra oryzae L.
3. C. oryzae is therefore much more susceptible to the gas than C. granaria.
4. M has a very strong after effect. In the case of C. granaria about 80 % were still alive immediately after fumigation with a dosage of 18.75 g; 24 hours later about 15 % were left and a week after fumigation all the insects were dead.
5. The results of fumigation with one fixed dose vary considerably. This variability always occurs in this kind of experiments. In order to obtain a clear idea of the dose required it is essential to carry out more than one series of experiments.

The values obtained were checked with the aid of larger, firmly constructed gassingboxes. These boxes have a capacity of 345 L and are made of three-ply wood 2 cm thick. The dimensions are 80 × 70 × 65 cm. The boxes contain a number of wooden grids. The loose door measures 60 × 70 cm and is screwed on the box by means of ten large winged nuts, while soft rubber is fitted round the edges to seal the box effectively. The boxes are provided with a wide exhaust tube, which reaches to the bottom of the box and is connected to a powerful exhauster (vide photograph No. 2).

There are two openings at the top closed by means of screw caps, through which fresh air enters when the exhauster is in operation. The tins containing the insects were placed on a wooden grid halfway up the boxes.

## EXPERIMENTS

with methallylchloride in gassingboxes with a capacity of 345 L. — Fumigation time 24 hours

CALANDRA GRANARIA L. (Ad.)

| Counted | Dose in grams per cub. m. | | | | Temperature |
|---|---|---|---|---|---|
| | 13.0 | 14.5 | 17.4 | 21.75 | |
| Dir. | 0 % | 8 % | 33 % | 100 % | |
| 24 h. | — | 74 | 87 | 100 | |
| 1 week | 69 | 98 | 100 | 100 | |

DITTO, CALANDRA ORYZAE L. (Ad.)

| Counted | Dose in grams per cub. m. | | | | | Temperature |
|---|---|---|---|---|---|---|
| | 12.6 | 13.0 | 14.5 | 17.4 | 21.75 | |
| Dir. | 98 % | 69 % | 80 % | 100 % | 100 % | |
| 24 hours | 100 | — | 100 | 100 | 100 | |
| 1 week | 100 | 100 | 100 | 100 | 100 | |

These results confirm those of previous experiments in smaller boxes.

The results are somewhat more favourable, which may probably be ascribed to relatively more gas having been adsorbed to the walls of the small gassing boxes, while it is also possible that small quantities of gas diffused through the walls of the small gassing boxes.

*Experiments with eggs, larvae and pupae.*

The question now is whether the other stages of the two species of Calandra can also be killed by fumigation with M.

As has already been mentioned these stages live inside the grains of corn and therefore are more difficult to reach.

In order to solve this question I carried out experiments in accordance with the following principle.

A great number of adults were introduced into a quantity of wheat. These were kept there for from six weeks to two months. It is then fairly certain that all stages are present in the wheat. If this is not the case it will become apparent from the experiments.

All the adults were then screened off and the wheat was divided into two equal parts. One batch was gassed, while the other was not. Then the two batches were screened daily whenever possible. The difference in numbers of the adults found was taken to represent the effect of the fumigation.

First series.

On June 7th 100 adults of Calandra granaria were introduced into wheat and were screened off again one week later on June 14th. The wheat therefore could contain at the most eggs and very young larvae. Half of the wheat treated in this manner was fumigated with a dose of 13 g of methallyl chloride per cub. m for 24 hours.

The adults which hatched later were screened off and the results are given in the table below:

| Date | Adults screened off | | Date | Adults screened off | |
|---|---|---|---|---|---|
| | non-fumig. | fumigated | | non-fumig. | fumigated |
| July 15 | 81 | 4 | July 27 | 7 | 3 |
| „ 16 | 31 | 1 | „ 28 | 7 | 1 |
| „ 19 | 31 | 1 | „ 29 | 3 | 2 |
| „ 20 | 13 | 0 | „ 30 | 3 | 3 |
| „ 21 | 13 | 5 | Aug. 2 | 3 | 2 |
| „ 22 | 14 | 9 | „ 3 | 1 | 1 |
| „ 23 | 8 | 5 | „ 4 | 2 | 1 |
| „ 26 | 11 | 10 | „ 5 | 2 | 1 |
| | | | „ 6 | 0 | 0 |

Total non-fumigated: 230 adults; fumigated: 49.

Second series.

Wheat which had contained about 500 adults for a period of 1½ months was screened, divided into two equal batches of which one was fumigated with a dose of 14.5 g of M per cub. m for 24 hours at an average temperature of 17° C.

The following results were obtained by screening daily:

| Date | Adults screened off | | Date | Adults screened off | |
|---|---|---|---|---|---|
| | non-fum. | fumigated | | non-fum. | fumigated |
| July 1 | 2 | 0 | Aug. 4 | 50 | 0 |
| „ 2 | 0 | 0 | „ 5 | 49 | 0 |
| „ 5 | 1 | 0 | „ 6 | 49 | 0 |
| „ 6 | 3 | 0 | „ 9 | 100 | 0 |
| „ 7 | 8 | 0 | „ 10 | 138 | 0 |
| „ 8 | 26 | 0 | „ 11 | 148 | 2 |
| „ 9 | 42 | 0 | „ 12 | 114 | 0 |
| „ 12 | 98 | 0 | „ 13 | 95 | 0 |
| „ 13 | 202 | 0 | „ 16 | 143 | 0 |
| „ 14 | 139 | 0 | „ 17 | 178 | 0 |
| „ 15 | 141 | 1 | „ 18 | 146 | 0 |
| „ 16 | 124 | 1 | „ 19 | 71 | 0 |
| „ 19 | 164 | 0 | „ 20 | 49 | 0 |
| „ 20 | 149 | 0 | „ 23 | 38 | 0 |
| „ 21 | 170 | 0 | „ 24 | 16 | 1 |
| „ 22 | 117 | 0 | „ 25 | 12 | 1 |
| „ 23 | 97 | 1 | „ 26 | 11 | 1 |
| „ 26 | 143 | 2 | „ 27 | 6 | 2 |
| „ 27 | 148 | 0 | „ 30 | 4 | 5 |
| „ 28 | 97 | 0 | Sept. 1 | 11 | 4 |
| „ 29 | 80 | 0 | „ 2 | 5 | 2 |
| „ 30 | 67 | 1 | „ 3 | 4 | 0 |
| Aug. 2 | 94 | 0 | „ 6 | 0 | 0 |
| „ 3 | 100 | 0 | | | |

Total non-fumigated: 3649 adults, fumigated: 24.

Third and fourth series.

775 g of wheat containing eggs, larvae and pupae of C. granaria and C. oryzae and a similar batch of 900 g were each gassed with a dose of 17.4 g of M per cub. m.

Parallel batches of 775 and 900 g each were not gassed.

Results of daily screening after fumigation:

| Date | Adults screened off serie 775 gr. | | Adults screened off serie 900 gr. | |
|---|---|---|---|---|
| | non-fum. | fumigated | non fum. | fumigated |
| Aug. 4 | 112 | 0 | 198 | 0 |
| „ 5 | 67 | 0 | 99 | 0 |
| „ 6 | 75 | 0 | 132 | 0 |
| „ 9 | 179 | 0 | 190 | 0 |
| „ 10 | 159 | 0 | 199 | 0 |
| „ 11 | 103 | 0 | 97 | 0 |
| „ 12 | 136 | 0 | 137 | 0 |
| „ 13 | 81 | 0 | 133 | 0 |
| „ 16 | 130 | 0 | 213 | 0 |
| „ 17 | 143 | 0 | 189 | 0 |
| „ 18 | 126 | 0 | 185 | 0 |
| „ 19 | 109 | 0 | 148 | 0 |
| „ 20 | 117 | 0 | 139 | 0 |
| „ 23 | 200 | 0 | 250 | 0 |
| „ 24 | 99 | 0 | 229 | 1 (C. gran.) |
| „ 25 | 122 | 0 | 236 | 0 |
| „ 26 | 126 | 0 | 242 | 0 |
| „ 27 | 141 | 0 | 182 | 0 |
| „ 30 | 238 | 0 | 437 | 0 |
| Sept. 1 | 194 | 1 (C. gran.) | 280 | 0 |
| „ 2 | 117 | 0 | 247 | 0 |
| „ 3 | 83 | 0 | 149 | 0 |
| „ 6 | 97 | 0 | 222 | 0 |
| „ 7 | 72 | 0 | 170 | 0 |
| „ 8 | 91 | 0 | 124 | 0 |
| „ 9 | 44 | 0 | 82 | 0 |
| „ 10 | 34 | 0 | 60 | 0 |
| „ 13 | 52 | 0 | 125 | 0 |
| „ 14 | 27 | 0 | 41 | 0 |
| „ 15 | 17 | 0 | 27 | 0 |

Third series non-fumigated total 3291 adults, fumigated 1.
Fourth series non-fumigated total 5162 adults, fumigated 1.

Conclusion (conditions as specified above):

1. Fumigation with a dose of 14.5 g of M per cub. m for 24 hours is sufficient to kill practically all the eggs, larvae and pupae of C. granaria and C. oryzae.
2. Fumigation with 17.5 g kills all these stages completely.
3. Fumigation with 18.5 g of M per cub. m for 24 hours at a temperature of about 18° C kills all stages of C. granaria and C. oryzae completely.
4. The insect is most resistant to the gas in the adult stage.

## II. INVESTIGATION INTO THE DISTRIBUTION OF THE GAS IN AN EMPTY SPACE

The vapours of M are three times as heavy as air and therefore the question arises how does it distribute itself in a space where no special measures have been taken (for instance mixing by means of a fan) to make the gas-air mixture homogeneous?

In order to ascertain this fourteen gauze bags each containing 50 C. oryzae were placed in a gassing box with a capacity of 345 L. Five of them were placed on the bottom of the box (one in each corner and one in the middle); 5 halfway up the box and four against the roof. A dose of 18.85 g per cub. m was introduced at the top of the box on a large sheet of filter paper. The temperature was 20° C and the duration of the fumigation six hours. The insects were examined 24 hours and one week after fumigation.
See table pages 23

*Conclusion:*

The gas in the box is distributed practically homogeneously. In the first series of experiments the effect is somewhat less

Percentage insects killed

| On the bottom of the box | | Halfway up the box | | Against the roof of the box | |
|---|---|---|---|---|---|
| after 24 hours | 1 week | after 24 hours | 1 week | after 24 hours | 1 week |
| 14 | 84 | 12 | 98 | 16 | 98 |
| 20 | 88 | 16 | 94 | 28 | 90 |
| 9 | 90 | 26 | 100 | 28 | 94 |
| 36 | 98 | 18 | 98 | 24 | 100 |
| 10 (middle) | 90 | 22 (middle) | 97 | | |

Second series. In these experiments the liquid was not evaporated on a large sheet of filter paper, but in a small petri dish with a small piece of filter paper.

| | | | | | |
|---|---|---|---|---|---|
| 36 | 100 | 36 | 96 | 36 | 94 |
| 34 | 94 | 38 | 94 | 44 | 100 |
| 28 | 98 | 35 | 91 | 28 | 98 |
| 30 | 86 | 38 | 93 | 26 | 97 |
| 40 (middle) | 100 | 60 (middle) | 98 | | |

pronounced, because the sheet of filter paper had adsorbed a good deal of gas. In fumigating trials in actual practice I had the opportunity to investigate the distribution of the gas in much larger spaces (page 60).

## III. INVESTIGATION INTO THE PENETRATION OF THE GAS IN WHEAT. FUMIGATION OF SILO'S

In order to ascertain whether the gas penetrates into the wheat sufficiently to kill the insects in the middle of the bags as well, a wooden frame measuring 45 × 45 × 50 cm was constructed and covered with jute sacking. This square bag was filled with about 80 kg of wheat in each experiment and it was ascertained what dose would be sufficient to kill Calandra granaria contained in a bag in the middle of the wheat. To this end the whole bag was placed in a 345 L. gassing box and was fumigated with different doses, at a fumigation period of 24 hours.

| Dose per cub.m. | dir. | 24 hours | 1 week | temp. |
|---|---|---|---|---|
| 24.7 g | 13 | 92 | 97 | 20° C |
| 29.0 ,, | — | 100 | 100 | 18° C |
| 36.3 ,, | 96 | 100 | 100 | 20° C |
| 43.5 ,, | 100 | 100 | 100 | 17° C |

In this case, therefore, about 25 g of M is sufficient to kill the adults.

The same experiment was repeated with the other stages of the Calandra species. To this end a small gauze bag of wheat containing all stages of the insect was placed in the middle of the large bag of wheat. A parallel sample remained unfumigated.

The dosage was 24.7 g per cub. m, duration of fumigation 24 hours, temperature 20° C. After fumigation the two samples containing the eggs, larvae and pupae were again screened practically every day.

| Date | Adults screened off | | Date | Adults screened off | |
|---|---|---|---|---|---|
| | non-fum. | fumigated | | non-fum. | fumigated |
| July 21 | 13 | 0 | Aug. 12 | 50 | 0 |
| ,, 22 | 5 | 0 | ,, 13 | 37 | 0 |
| ,, 23 | 10 | 0 | ,, 16 | 44 | 1 |
| ,, 26 | 13 | 0 | ,, 17 | 22 | 0 |
| ,, 27 | 26 | 0 | ,, 18 | 38 | 0 |
| ,, 28 | 22 | 0 | ,, 19 | 27 | 0 |
| ,, 29 | 29 | 2 | ,, 20 | 23 | 0 |
| ,, 30 | 22 | 1 | ,, 23 | 54 | 0 |
| Aug. 2 | 31 | 0 | ,, 24 | 22 | 0 |
| ,, 3 | 42 | 0 | ,, 25 | 42 | 1 |
| ,, 4 | 34 | 1 | ,, 26 | 33 | 0 |
| ,, 5 | 29 | 2 | ,, 27 | 24 | 0 |
| ,, 6 | 47 | 0 | ,, 30 | 32 | 0 |
| ,, 9 | 57 | 0 | Sept. 1 | 36 | 0 |
| ,, 10 | 53 | 0 | ,, 2 | 31 | 0 |
| ,, 11 | 40 | 0 | | | |

Total non-fumigated 988 adults, fumigated 8 adults.

In order to obtain better idea still of the distribution of the gas in a large quantity of wheat, one of the 80 L gassing boxes already described was entirely filled with wheat, and five small gauze bags each containing 50 Calandra granaria were placed on the bottom of the box, five halfway up the box and five against the roof.

The bags were divided over the box as follows:

| Bottom | | | Middle | | | Top | | |
|---|---|---|---|---|---|---|---|---|
| 3 | | 4 | 8 | | 9 | 13 | | 14 |
| | 5 | | | 10 | | | 15 | |
| 2 | | 1 | 7 | | 6 | 12 | | 11 |

The gas was introduced in one of the top corners, immediately above bag No. 11. Bags No. 6 and 1 are situated immediately below. The dosage for this gassing box was 3 g. Duration of fumigation 24 hours, temperature 20° C.

The insects were examined immediately after fumigation, 24 hours later and a week later. The figures represent the percentage of insects killed.

| No. | Dir. | 24 h. | 1 week |
|---|---|---|---|
| 1 | 86 | 100 | 100 |
| 2 | 10 | 59 | 86 |
| 3 | 4 | 8 | 40 |
| 4 | 2 | 42 | 94 |
| 5 | 12 | 94 | 100 |
| 6 | 96 | 100 | 100 |
| 7 | 6 | 17 | 68 |
| 8 | 0 | 11 | 36 |
| 9 | 6 | 22 | 78 |
| 10 | 15 | 68 | 98 |
| 11 | 61 | 96 | 100 |
| 12 | 2 | 4 | 24 |
| 13 | 4 | 7 | 20 |
| 14 | 2 | 5 | 23 |
| 15 | 30 | 37 | 61 |

The results of this experiment have been conveniently arranged in figure 1. The figures in this drawing represent the percentage of kill one week after fumigation. The positions of these figures correspond to the positions of the bags containing Calandra. This illustrates very clearly that the gas immediately descended to the bottom and spread there; also that the concentration must have been weaker halfway up and reached a minimum at the top.

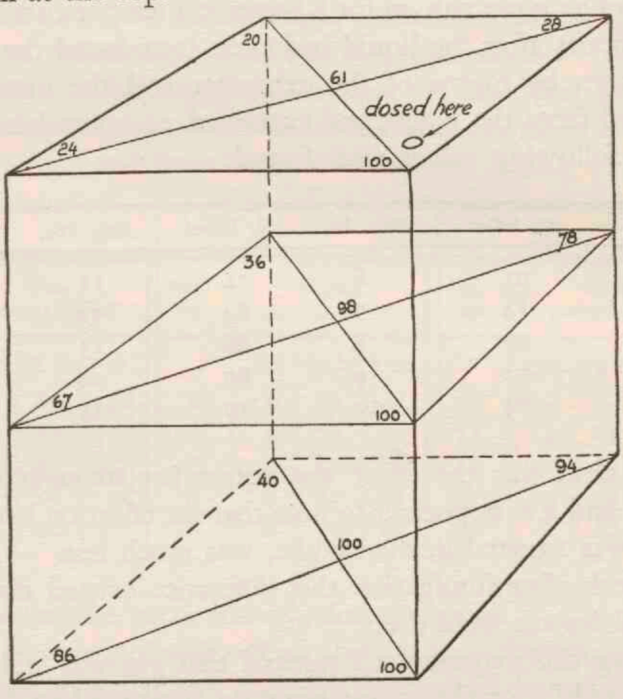



Fig. 1

For reasons which are described further on experiments were also carried out to examine the penetration during a shorter period of fumigation. The same square bag was used for this purpose filled with 83 kg of wheat. Five small gauze bags each containing 25 Calandra granaria were placed on the bottom, 5 halfway up and 5 on top of the wheat. The positions of the bags were:

| Top | | Middle | | Bottom | |
|---|---|---|---|---|---|
| 4 | 3 | 9 | 8 | 14 | 13 |
| 5 | | 10 | | 15 | |
| 1 | 2 | 6 | 7 | 11 | 12 |

The square bag was covered with jute sacking and placed in a gassing box with a capacity of 345 L and fumigated with a dose of 72 g per cub. m for 6 hours at a temperature of 20° C.

Six hours after the liquid had been introduced the gas was withdrawn by means of the exhauster and the insects were removed from the wheat and examined 24 hours later.

The following values were found:

| Bag. No. | % killed | Bag. No. | % killed | Bag. No. | % killed |
|---|---|---|---|---|---|
| 1 | 91 | 6 | 72 | 11 | 96 |
| 2 | 84 | 7 | 84 | 12 | 96 |
| 3 | 88 | 8 | 80 | 13 | 84 |
| 4 | 72 | 9 | 80 | 14 | 96 |
| 5 | 84 | 10 | 20 | 15 | 93 |

It is clear that the effect was somewhat stronger near the bottom and it is important to note that the effect on bag No. 10, which was situated in the middle, was much less.

A week after fumigation this difference existed no longer, since all insects were dead.

During this experiment I noticed that gas was still present in the middle of the wheat after the gassing box had been exhausted. The procedure was therefore as follows: The gas penetrated into the quantity of wheat very slowly reaching the middle bag after some time. Fumigation was stopped 6 hours after the liquid had been introduced. At this moment the bags containing the insects were removed from the wheat.

In actual practice the procedure is different. If a storeroom containing bags of wheat or other products is fumigated, the gas penetrates to the middle of the bag very slowly in the same way as in the experiment. When subsequently the room is ventilated, the gas which is present in the bags diffuses very slowly from them. Inside the bags fumigation therefore continues even after ventilation has been started.

In order to imitate these conditions in the laboratory, the experiment was repeated and modified as follows. The square bag of wheat was removed from the box at the end of 6 hours, but the little bags containing the insects were left in the wheat for another 24 hours. Furthermore, a smaller dose was applied, so that any differences would not be imperceptible owing to all the insects succumbing. In this case the dose was 40 g per cub. m. Temperature 20° C. The insects were examined immediately after they had been removed from the wheat, 72 hours later and one week later. The following results were obtained:

| Bag. No. | Top percent killed | | | Bag. No. | Middle percent killed | | | Bag. No. | Bottom percent killed | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | dir. | 72 h. | 1 w. | | dir. | 72 h. | 1 w. | | dir. | 72 h. | 1 w. |
| 1 | 8 | 80 | 98 | 6 | 15 | 76 | 93 | 11 | 4 | 74 | 96 |
| 2 | 14 | 84 | 100 | 7 | 4 | 76 | 96 | 12 | 14 | 67 | 94 |
| 3 | 30 | 82 | 100 | 8 | 2 | 80 | 96 | 13 | 7 | 67 | 93 |
| 4 | 46 | 84 | 98 | 9 | 4 | 73 | 98 | 14 | 14 | 78 | 98 |
| 5 | 24 | 98 | 100 | 10 | 4 | 70 | 92 | 15 | 1 | 62 | 88 |

Now it may be seen, indeed, that the effect on the middle bag No. 10 does not differ from that on the other bags.

This experiment shows that the problem of the penetrating capacity of a gas is not of such importance as is generally believed. If a gas takes a long time to penetrate, it also takes a long time to escape. The final result is by no means below that of a quickly penetrating gas.

Of course, the gas should penetrate quickly enough to reach the middle of the bags within the fumigation time.

In any case the penetration of M into bags of wheat is sufficient. This is not the case, however, for the fumigation of silos. These may be up to 30 m high, so that the gas must penetrate through a very thick layer of wheat to reach all the insects.

Experiments were carried out in a glass tube 3 m long and 7.5 cm in diameter. The total capacity is about 11.5 L.

This tube was filled with wheat. Small gauze bags each containing 25 C. granaria were placed at distances of 50 cm. Altogether there were 6 bags, so the top bag was situated 50 cm below the surface of the wheat. It was found that even a dose of 260 g of M per cub. m (calculated on the total capacity of the tube of 11.5 L) was insufficient to reach the second bag from the top. The insects in the first bag, situated 50 cm below the surface, were already killed by a dose of 43.5 g per cub. m.

A duplicate experiment was carried out in a tube 1.50 m long, the diameter being the same as that of the other tube, which was filled with glass beads. It was found that 260 g per cub. m was only just sufficient to kill all the insects in the bags Although in the case of glass beads only adsorption comes into play the required dose is already very high.

These experiments show that for silos up to 30 m high effective fumigation with M is impossible by merely introducing the gas above the surface of the wheat.

The only solution in such cases is to pump the gas through the wheat, as is done, inter alia, with areginal.

In order to try this out the glass tube was prepared once more with six bags of wheat each containing 25 C. granaria, and a pump with a capacity of 2 L per minute was connected to it. A Wulff bottle which served as evaporation space was also inserted in the system. The liquid was introduced into the bottle. The current of gas passed from the bottom of the tube to the top. The dose was fixed at 120 g per cub. m, duration of fumigation 6 hours, temperature 20° C. In this experiment all the insects were killed in the column of wheat. The dose of 120 g per cub. m should not be regarded as a minimum value.

This experiment shows that circulation of the gas by means of a pump is the right solution. Vide Kunike (31).

Thus the *penetrating* capacity of M is very good, except when very thick layers are concerned in which case special technical provisions should be made.

## IV. DETERMINATION OF THE EFFECT OF THE PRESENCE OF THE PRODUCTS WHICH ARE TO BE FUMIGATED ON THE DOSE REQUIRED AND OF THE EFFECT OF THE GAS ON THE QUALITY OF THE PRODUCTS

The first part of this investigation provided an answer to the question as to in how far M is able to kill insects in empty spaces, the dose being determined at which the kill was 100 %.

The presence of goods, in this case stores of grain, alters the prevailing conditions, however, and we shall have to see what influence this has on the effect of the gas with respect to the insects. It is clear that the presence of goods reduces the quantity of air in the space. Page and Lubatti (32) found that the quantity of air in one cubic metre of wheat is about 400 litres. So the intergranular space is 400 L. If the same quantity of gas were applied in 1 cub. m of empty space and in 1 cub. m. of wheat the concentration would therefore become 2½ times as high in the latter case. For this reason Lepigre (33) regards a chamber containing wheat as being composed of one part filled with material and an empty part; he calculates the dose required for each part separately. Thus for ethene oxide he recommends "23 grams per cub. m. of wheat and 50 grams per cub. m. of actual space". So he specifies a smaller dose for 1 cub. m. of wheat than for 1 cub m. of empty space.

The second influence, i.e. of the presence of the product on the effect of the gas, will, in this case, not be evident. For, the product deactivates part of the gas owing to adsorption and as a result of the gas dissolving in constituents of the product or chemically combining with it. Therefore, on the one hand the presence of the product in the space causes a rise in the concentration, because the actual space becomes smaller, on the other, a reduction owing to absorption etc.

We therefore get:

a. An increase }
b. A decrease } of the concentration

If the same dose is applied the result may therefore be that:

1. The average concentration in the filled space remains higher than in an empty one ($a > b$);
2. The average concentration of gas in the filled space remains lower than in an empty one ($a < b$);
3. The average concentration remains the same ($a = b$).

This refers to the influence of the presence of goods on the dose required.

The effect of the gas on the quality of the goods is of far greater importance. There is little information to be found on this point in the literature on the subject. Generally the materials for combating insects are only tested for their insecticidal effect in fumigation chambers containing nothing but the insects. In many cases experiments are also carried out to determine the effect of the gas on the germinative power of seeds, but it was only in exceptional cases that its effect on the odour and taste of the products fumigated was investigated.

Roark and Cotton (21) carried out laboratory experiments with fumigants in spaces partially filled with products. They used 500 ml. Erlenmeyers. They placed ten insects on the bottom and poured 250 ml. or about 200 g of wheat over them.

In U.S. Dept. Agric. Bull. No. 1313 experiments are referred to with fumigants in the presence of a certain quantity of wheat. In the same Bulletin a number of milling and baking tests are reported on. It is said that flour often retains the odour of carbon disulphide and that the flour ground from fumigated wheat has less good baking qualities. Ethyl acetate in a not quite pure condition also impairs the odour and taste.

Flury (39) states that ethene oxide has an adverse effect upon the taste of some products.

We therefore see that information on this point in the literature is rather sparse and in those cases where an investigation was carried out it was rather superficial. On the other hand, it is a much discussed point in actual practice. When fumigation is discussed with managers of warehouses, their first enquiry is inevitably about the effect of fumigation on the quality of their goods.

I therefore decided to carry out an accurate and thorough investigation into the influence of fumigation on the odour and taste of the products.

In order to find out whether M *can* affect the odour and taste under very unfavourable conditions, I carried out the following experiment:

Two kg of wheat were fumigated in a 345 L gassing box with a dose corresponding to 72.5 g per cub. m for 24 hours and at a temperature averaging 18° C. After fumigation the wheat was aired for 24 hours. At the end of that period there was nothing abnormal about it. The wheat was then ground to flour. This flour had a slightly musty smell. The bread baked from the flour looked perfectly normal, but the mouldy smell persisted and the taste of the bread was also affected.

Under certain conditions it is therefore *possible* that M has a detrimental effect on the odour and taste, which property it has in common with many other fumigants. The problem is therefore, what procedure must be followed to avoid this with absolute certainty.

*The influence of the "filling" on possible change in quality.*

To gain some information on the problem just mentioned, the influence of the "filling" was first investigated. By "filling" I understand the number of kilograms of product in one cubic metre of space.

It is by no means the same thing whether 100 kg of wheat are fumigated in one cub. m or in ten, under the same conditions as regards the dose applied, fumigation time and temperature. In the latter case the absolute quantity of gas is much larger, the ratio between the quantity of gas and the quantity of product more unfavourable. It is therefore possible that in this case more gas is absorbed by the product than when the latter is in a smaller space. To make this clear I carried out a series of experiments.

Glass jars of 3.1 L capacity were used, with metal lids fitting with a bayonet catch. A series of these jars was filled with 0.50, 0.75, 1.00, 1.25, 1.50, 1.75 and 2 kg of wheat, respectively. On the bottom of each jar, underneath the wheat were placed gauze bags each containing 50 Calandra granaria.

It was then determined how much gas was needed in each case to kill the insects. A small aperture was pierced through the lids to admit the liquid. Underneath this aperture a glass dish with filter paper was placed. After the liquid had been introduced, the opening was sealed with surgical plaster which was then coated with cellon lacquer. The edge of the lid was also secured with surgical plaster. The jars stood in a room with a temperature of 18—19° C. When recording the results the dose applied is given in ml per kg of wheat and ml per jar. The liquid was dosed by means of a 1 ml pipette graduated in 0.01 ml.

| kg of wheat | M per kg in ml | M per jar in ml | Mortality 24 hours | Mortality 1 week |
|---|---|---|---|---|
| 2 | 0.025 | 0.050 | 34 | 73 |
| 2 | 0.025 | 0.050 | 22 | 73 |
| 2 | 0.030 | 0.060 | 60 | 98 |
| 2 | 0.030 | 0.060 | 42 | 92 |
| 2 | 0.040 | 0.080 | 72 | 100 |
| 2 | 0.040 | 0.080 | 86 | 100 |
| 2 | 0.050 | 0.100 | 94 | 100 |
| 2 | 0.075 | 0.150 | 100 | 100 |

| kg of wheat | M per kg in ml | M per jar in ml | Mortality 24 hours | Mortality 1 week |
|---|---|---|---|---|
| 2 | 0.100 | 0.200 | 100 | 100 |
| 1.75 | 0.025 | 0.044 | 16 | 65 |
| 1.75 | 0.030 | 0.053 | 36 | 70 |
| 1.75 | 0.030 | 0.053 | 49 | 92 |
| 1.75 | 0.040 | 0.070 | 96 | 100 |
| 1.75 | 0.040 | 0.070 | 73 | 100 |
| 1.75 | 0.050 | 0.088 | 92 | 100 |
| 1.75 | 0.075 | 0.131 | 100 | 100 |
| 1.75 | 0.100 | 0.175 | 100 | 100 |
| 1.50 | 0.030 | 0.045 | 40 | 83 |
| 1.50 | 0.030 | 0.045 | 51 | 100 |
| 1.50 | 0.040 | 0.060 | 94 | 100 |
| 1.50 | 0.040 | 0.060 | 96 | 100 |
| 1.50 | 0.050 | 0.075 | 94 | 100 |
| 1.50 | 0.075 | 0.113 | 100 | 100 |
| 1.50 | 0.100 | 0.150 | 100 | 100 |
| 1.25 | 0.050 | 0.063 | 69 | 90 |
| 1.25 | 0.050 | 0.063 | 100 | 100 |
| 1.25 | 0.075 | 0.094 | 96 | 100 |
| 1.25 | 0.100 | 0.125 | 100 | 100 |
| 1.00 | 0.050 | 0.050 | 62 | 94 |
| 1.00 | 0.050 | 0.050 | 60 | 100 |
| 1.00 | 0.060 | 0.060 | 100 | 100 |
| 1.00 | 0.075 | 0.075 | 98 | 100 |
| 1.00 | 0.075 | 0.075 | 100 | 100 |
| 1.00 | 0.100 | 0.100 | 100 | 100 |
| 0.75 | 0.040 | 0.030 | 25 | 40 |
| 0.75 | 0.050 | 0.038 | 30 | 49 |
| 0.75 | 0.050 | 0.038 | 27 | 71 |
| 0.75 | 0.050 | 0.038 | 43 | 80 |
| 0.75 | 0.060 | 0.045 | 36 | 82 |
| 0.75 | 0.075 | 0.056 | 98 | 100 |
| 0.75 | 0.100 | 0.075 | 100 | 100 |
| 0.50 | 0.050 | 0.025 | 24 | 52 |
| 0.50 | 0.075 | 0.038 | 63 | 94 |
| 0.50 | 0.075 | 0.038 | 12 | 61 |
| 0.50 | 0.085 | 0.043 | 62 | 97 |
| 0.50 | 0.100 | 0.050 | 100 | 100 |

This series displays a few irregularities, presumably due to the difficulty of dosing such small quantities. It is shown, however, that with a filling of 2 kg about 0.080 ml of M per jar, or 0.040 ml per kg is required, as against 0.045 ml per jar, or 0.090 ml per kg with a filling of 0.50 kg. The other values lie between these figures. The dose per jar, i.e. per unit of fumigation space therefore *decreases* in proportion as there is less wheat present, whereas the dose calculated per kg of wheat *rises* considerably if the filling is decreased.

At a filling of 0.50 kg per jar the most gas is needed relatively. Let us see whether in this case the odour and taste are affected.

It was found that, with a dose of 0.100 ml per jar, the taste of the bread baked from this wheat was slightly affected. The dose required to kill the insects was 0.045 ml; the dose that brought about a noticeable change in the taste was 0.100 ml Therefore,

the minimum dose is 0.045 ml
„ maximum „ „ 0.100 ml.

It now remains to be seen whether this margin becomes *wider* if the filling of the fumigation chamber is increased. This I investigated by fumigating equal quantities of wheat and other products under the same conditions as regards the dose, time and temperature, in a 3.1 litres jar (large filling) and a gassing box of 345 litres (small filling). It was not possible to observe any difference with any measure of certainty, however; besides, taste is such a subjective matter. At any rate there was not a marked difference. Some other means ought therefore to be found for increasing the margin.

## V. INFLUENCE OF THE FUMIGATION TIME ON ANY CHANGE IN QUALITY

As the influence on the quality was not sufficiently removed by the above means, the influence of the fumigation *time* was examined. For this purpose experiments were made in a series of 3.1 litres jars, each containing 2 kg of wheat, in the manner described above. But in these tests the fumigation time was three hours, the temperature averaging 18° C. The dose is again given in ml per kg of wheat and in ml per jar. The insects subjected to the test were again Calandra granaria, 50 at a time.

First series

| ml M per kg | ml M per jar | Mortality | |
|---|---|---|---|
| | | 24 hours | 1 week |
| 0.3 | 0.6 | 100 | 100 |
| 0.3 | 0.6 | 100 | 100 |
| 0.3 | 0.6 | 100 | 100 |
| 0.2 | 0.4 | 80 | 100 |
| 0.2 | 0.4 | 94 | 100 |
| 0.2 | 0.4 | 90 | 100 |
| 0.15 | 0.3 | 33 | 92 |
| 0.15 | 0.3 | 32 | 95 |
| 0.10 | 0.2 | 8 | 86 |
| 0.10 | 0.2 | 4 | 88 |

Second series

| | | | |
|---|---|---|---|
| 0.3 | 0.6 | 100 | 100 |
| 0.3 | 0.6 | 100 | 100 |
| 0.25 | 0.5 | 87 | 100 |
| 0.25 | 0.5 | 98 | 100 |
| 0.20 | 0.4 | 82 | 100 |
| 0.20 | 0.4 | 79 | 100 |
| 0.15 | 0.3 | 43 | 98 |
| 0.15 | 0.3 | 65 | 100 |
| 0.10 | 0.2 | 33 | 83 |
| 0.10 | 0.2 | 13 | 48 |
| 0.05 | 0.1 | 4 | 19 |
| blanco | blanco | 0 | 12 |
| blanco | blanco | 8 | 11 |

It is evident from these series that a dose of a little over 0.3 ml per 3.1 litres jar containing 2 kg of wheat is sufficient to kill the Calandra. The tests with a gassing time of 24 hours showed that under the same conditions 0.080 ml was required. Therefore:

Fumigation time of 24 hours requires 0.080 ml
,, ,, ,, 3 ,, ,, just over 0.3 ml

This reveals the surprising fact that when the fumigation time is reduced to one eighth, only four times as large a dose is required to produce the same effect.

According to Peters (30) the effect of a gas may be expressed as the product of the concentration applied and the time of exposure. According to Haber this product in different cases amounts to a constant value if related to the same mortality. (Haber's law: $c.t = K$). So, if the time t is reduced, the concentration c must be increased accordingly. The results of my investigations show that this law does not hold good in the case of M. In how far this applies will be dealt with in a subsequent chapter.

The experiments with wheat in jars were continued upon a series in which the filling was varied; the fumigation time invariably being three hours.

| kg of wheat per jar | M per kg in ml | M per jar in ml | Mortality | |
|---|---|---|---|---|
| | | | 24 hours | 1 week |
| 2 | 0.16 | 0.32 | 86 | 100 |
| 1.75 | 0.17 | 0.30 | 96 | 100 |
| 1.75 | 0.17 | 0.30 | 90 | 100 |
| 1.50 | 0.18 | 0.27 | 93 | 100 |
| 1.50 | 0.18 | 0.27 | 80 | 100 |
| 1.25 | 0.20 | 0.25 | 90 | 100 |
| 1.25 | 0.20 | 0.25 | 72 | 100 |
| 1.00 | 0.24 | 0.24 | 86 | 100 |
| 1.00 | 0.24 | 0.24 | 76 | 100 |
| 0.75 | 0.28 | 0.21 | 54 | 100 |
| 0.75 | 0.28 | 0.21 | 50 | 98 |
| 0.50 | 0.36 | 0.18 | 27 | 97 |
| 0.50 | 0.36 | 0.18 | 37 | 99 |

This series again proves very clearly that the required dose, calculated per kg of wheat, increases in proportion as the filling is smaller and that this dose, calculated per jar, decreases in proportion as the filling is reduced.

It is now essential to know what happens to the taste and odour of the goods in a fumigation time of three hours. It had already been found that wheat fumigated in a jar with a filling of ½ kg and with 0.200 ml of M per kg, fumigation time 24 hours, produces bread with a faintly different taste. In this connection I made an experiment in which some jars containing ½ kg of wheat were dosed with 0.8 ml per jar or 1.6 ml per kg; fumigation time three hours. The bread baked from this was quite normal. Now the evaporation time of 0.8 ml of M is comparatively long in relation to the total fumigation time. This was checked in a test allowing a fumigation time of 3½ hours, after it had been ascertained that the liquid evaporates within half an hour. The bread was again quite normal. We therefore now have the following data:

For fumigation of ½ kg of wheat in a 3.1 litres jar the dose required is with a *fumigation time of* 24 *hours*:

the minimum dose (insects) is 0.090 ml per kg of wheat
„ maximum „ (taste) „ 0.200 „ „ „ „ „

with a *fumigation time of* 3 *hours:*

the minimum dose (insects) is 0.36 ml per kg of wheat
„ maximum „ (taste) $>$ 1.60 „ „ „ „ „

With a fumigation time of 24 hours the taste is impaired under these conditions if the dose is slightly more than doubled. With a fumigation time of three hours the taste is not affected if slightly more than four times the dose is applied. This proves, therefore, that a short fumigation time offers considerable advantages as compared with a longer time. This does not only save time, but the risk of the goods being affected is practically reduced to nil. Products of a susceptible quality can therefore also be fumigated if a shorter fumigation time is taken.

## VI. EFFECT UPON EGGS, LARVAE AND PUPAE AFTER SHORT FUMIGATION TIME

It is certainly also important to study the effect of the gas upon the eggs, larvae and pupae when a fumigation time of three hours is allowed. For this purpose 3.1 litres were again used, containing 2 kg of wheat infested by eggs, larvae and pupae. To be able to make a comparison a test was also made with areginal, while an equal quantity was left unfumigated. The dose of M was 0.16 ml per kg of wheat, or 0.32 ml per jar and of areginal 0.425 ml per kg or 0.85 ml per jar.

After fumigation the three samples were screened daily as often as possible and the adults developed were counted. The results were as follows:

| Date | Blank | Areginal | M | Date | Blank | Areginal | M |
|---|---|---|---|---|---|---|---|
| Jan. 3 | 54 | 0 | 0 | Jan. 24 | 63 | 0 | 0 |
| „ 4 | 40 | 0 | 0 | „ 25 | 67 | 1 | 0 |
| „ 5 | 15 | 0 | 0 | „ 26 | 39 | 1 | 0 |
| „ 6 | 23 | 0 | 0 | „ 27 | 34 | 0 | 0 |
| „ 7 | 21 | 1 | 0 | „ 28 | 69 | 5 | 0 |
| „ 10 | 66 | 7 | 0 | „ 31 | 64 | 2 | 0 |
| „ 11 | 75 | 10 | 0 | Febr. 2 | 99 | 7 | 0 |
| „ 12 | 39 | 9 | 0 | „ 3 | 30 | 1 | 0 |
| „ 13 | 40 | 8 | 0 | „ 4 | 22 | 0 | 0 |
| „ 14 | 35 | 2 | 0 | „ 7 | 36 | 0 | 0 |
| „ 17 | 70 | 6 | 0 | „ 8 | 9 | 0 | 0 |
| „ 18 | 36 | 3 | 0 | „ 9 | 7 | 0 | 0 |
| „ 19 | 30 | 3 | 0 | „ 10 | 8 | 2 | 0 |
| „ 20 | 12 | 0 | 0 | „ 11 | 7 | 1 | 0 |
| „ 21 | 14 | 4 | 0 | „ 14 | 12 | 0 | 0 |

Blank: 1136 adults, areginal 73 adults, M 0 adults. The dose of areginal was therefore insufficient, whereas M had killed all the stages.

During the fumigation gauze bags containing 50 adults of Calandra granaria were laid on the bottom of the jars of infested wheat.

Result with M: 28 % dead immediately after gassing, 100 % dead two days later. With areginal: all the weevils seemed to be dead immediately after fumigation, two days later 80 % seemed to be dead and a week after the gassing 68 %. The effect of areginal is therefore the reverse of M: immediately after fumigation all the insects seem to be dead, but many of them revive afterwards.

M does not kill the insects at once, but has a very strong *after-effect*; areginal causes a serious *knock-down*, but the insects revive. In this respect ethene oxide resembles M, whereas carbon disulphide has a similar effect to Areginal.

## VII. INFLUENCE OF THE FILLING ON THE DOSE REQUIRED

In the above test series it is shown that the dose per jar *drops* according as it contains less wheat and that the dose calculated per kg of wheat rises according as less product is present in it.

This would lead to the conclusion in practice, too, the dose should be adjusted to the filling of the space. However, I was not quite satisfied with the method with the glass jars, because the *layer thickness* of the wheat differs. I therefore cast about for an essentially similar method with the same layer thickness in all cases.

To this end I used tins *differing* in capacity but containing *the same quantity* of wheat, thus varying the fumigation space instead of the quantity of wheat.

Seven tin cans, 15 cm in diameter and having a capacity of 10, 5, 3.3, 2.5, 2.0, 1.7 and 1.4 litres (see photograph 4) were filled with 1 kg of wheat each. Calculated per cubic metre, this means a filling of the various tins as tabulated below.

| Capacity tin | Filling per cub. m |
|---|---|
| 10 litres | 100 kg |
| 5 ,, | 200 ,, |
| 3.3 ,, | 300 ,, |
| 2.5 ,, | 400 ,, |
| 2.0 ,, | 500 ,, |
| 1.7 ,, | 600 ,, |
| 1.4 ,, | 700 ,, |

I used these tins in the same way as described above for the jars; fumigation time 6 hours, temperature 20° C. The results are given below. The mortality was determined 24 hours after gassing; the doses are stated in ml per tin.

| Tin | Cap. in l | dos. | mort. | d | m | d | m | d | m | d | m | d | m | | d | m | d | m | d | m |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 10 | 0.28 | 12 | 0.35 | 46 | 0.42 | 86 | 0.42 | 66 | 0.52 | 76 | 0.52 | 74 | | 0.50 | 82 | 0.50 | 78 | 0.50 | 78 |
| 2 | 5 | 0.22 | 85 | 0.26 | 92 | 0.28 | 96 | 0.26 | 94 | | | 0.26 | 65 | | 0.25 | 82 | | | | |
| 3 | 3.3 | 0.18 | 98 | 0.18 | 95 | 0.18 | 79 | 0.17 | 79 | 0.17 | 66 | 0.17 | 66 | | 0.17 | 83 | 0.17 | 83 | 0.17 | 79 |
| 4 | 2.5 | 0.15 | 100 | 0.14 | 100 | 0.14 | 100 | 0.13 | 96 | | | 0.13 | 59 | | 0.13 | 86 | | | | |
| 5 | 2 | 0.13 | 100 | 0.11 | 93 | 0.11 | 98 | 0.10 | 92 | 0.10 | 36 | 0.10 | 66 | | 0.10 | 76 | 0.10 | 74 | 0.10 | 70 |
| 6 | 1.7 | 0.12 | 100 | 0.09 | 52 | 0.09 | 100 | 0.08 | 87 | | | 0.08 | 40 | | 0.08 | 58 | | | | |
| 7 | 1.4 | 0.10 | 100 | 0.08 | 97 | 0.08 | 100 | 0.07 | 87 | 0.07 | 74 | 0.07 | 65 | | 0.07 | 76 | 0.07 | 78 | 0.07 | 70 |

As is usual in tests on insects, the results show rather considerable spreading. This is the least in the last three series, which were carried out with the most scrupulous accuracy.

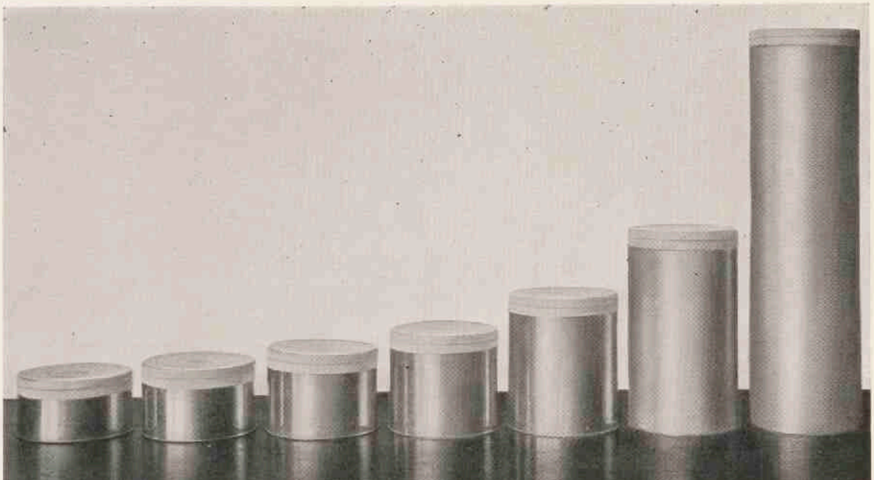
The conclusion is that, to get the same mortality, the approximate requirements are:

| Tin | Capacity in litres | Dose p. tin | Dose per cub. m in ml |
|---|---|---|---|
| 1 | 10 | 0.50 | 50 |
| 2 | 5 | 0.25 | 50 |
| 3 | 3.3 | 0.17 | 51 |
| 4 | 2.5 | 0.13 | 52 |
| 5 | 2 | 0.10 | 50 |
| 6 | 1.7 | 0.08 | 48 |
| 7 | 1.4 | 0.07 | 49 |

In other words: with a different filling there is no appreciable difference in the dose required. This amounts to about 50 ml in all cases.

The difference found in the tests with glass jars of the same capacity and differing in filling was, therefore, actually caused by the differences in thickness of the wheat layers; this was eliminated in the tins.

3. Series of jars filled with wheat



4. Series of tins


5. Dug out Delphiniums, three days after fumigation. Fumigated with M and with T gas (90 % ethene oxide + 10 % $CO_2$) for 24 hours, dose 19 g per cub. m

The method with the glass jars provides an excellent means of comparing the rate of penetration of two different gases.

In the case of wheat the filling has no influence on the dose, so that the absorption is equal to the quantity of gas displaced by the wheat (a = b, page 32).

The dose required for the fumigation of wheat is therefore 50 ml per cub. m, i.e. 46 g per cub. m at a fumigation time of 6 hours and a temperature of 20° C.

These facts were tested in two series of tests with tins, with a dose of 40 ml per cub. m, in which the insects were examined three times:

| Capacity in litres | Dose | Per cent killed in | | | Capacity in litres | Dose | Per cent killed n | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 24 h. | 2 days | 1 w. | | | 24 h. | 2 days | 1 w. |
| 10 | 0.40 | 47 | 79 | 100 | 10 | 0.40 | 32 | 78 | 100 |
| 5 | 0.20 | 50 | 82 | 100 | 5 | 0.20 | 37 | 87 | 100 |
| 3.3 | 0.13 | 32 | 64 | 98 | 3.3 | 0.13 | 20 | 78 | 100 |
| 2.5 | 0.10 | 36 | 80 | 97 | 2.5 | 0.10 | 26 | 80 | 96 |
| 2 | 0.08 | 40 | 78 | 100 | 2 | 0.08 | 40 | 84 | 98 |
| 1.7 | 0.07 | 42 | 80 | 98 | 1.7 | 0.07 | 29 | 73 | 97 |
| 1.4 | 0.06 | 18 | 58 | 96 | 1.4 | 0.06 | 32 | 89 | 100 |

This confirms that in the case of wheat fumigation the filling has hardly any influence on the dose required. This is even more clearly evident in comparison with wheat *flour*.

Each tin contained ½ kg of wheat flour. The bags of Calandra were laid under the flour on the bottom of the tin. Some tentative tests were first carried out with tins of the *same* capacity.

| Capacity in litres | Dose per tin | Per cent killed in | | |
|---|---|---|---|---|
| | | 24 hours | 3 days | 1 week |
| 3.3 | 0.27 | 36 | 90 | 92 |
| 3.3 | 0.33 | 55 | 100 | 100 |
| 3.3 | 0.40 | 78 | 100 | 100 |

Subsequently, three tins of *different* capacity were used, the dose being 100 ml per cub. m.

| Capacity in litres | Dose per tin | Killed in | | |
|---|---|---|---|---|
| | | 24 hours | 2 days | 1 week |
| 5 | 0.50 | 78 | 100 | 100 |
| 3.3 | 0.33 | 18 | 78 | 100 |
| 2.5 | 0.25 | 20 | 56 | 98 |

In this test it is shown that, in the case of flour, the filling did influence the results. Calculating the filling per cub. m and taking the mortality after two days, we find:

| Capacity tin | Filling per cub. m in kg | Per cent killed |
|---|---|---|
| 5 | 100 | 100 |
| 3.3 | 150 | 78 |
| 2.5 | 200 | 56 |

With a larger filling the effect is therefore smaller. This result was tested on the whole series of tins, dose 100 ml per cub. m.

| Capacity in litres | Filling per cub. m in kg | Dose per tin in ml | 24 hours | 2 days | 1 week |
|---|---|---|---|---|---|
| 10 | 50 | 1 | 93 | 100 | 100 |
| 5 | 100 | 0.50 | 68 | 100 | 100 |
| 3.3 | 150 | 0.33 | 10 | 81 | 98 |
| 2.5 | 200 | 0.25 | 29 | 79 | 100 |
| 2 | 250 | 0.20 | 0 | 26 | 74 |
| 1.7 | 300 | 0.17 | 0 | 14 | 80 |
| 1.4 | 350 | 0.14 | 0 | 8 | 78 |
| 10 | 50 | 1.00 | 98 | 100 | 100 |
| 5 | 100 | 0.50 | 68 | 100 | 100 |
| 3.3 | 150 | 0.33 | 26 | 86 | 100 |
| 2.5 | 200 | 0.25 | 30 | 78 | 100 |
| 2 | 250 | 0.20 | 4 | 48 | 92 |
| 1.7 | 300 | 0.17 | 4 | 20 | 84 |
| 1.4 | 350 | 0.14 | 0 | 16 | 74 |

The result obviously decreases with increasing filling (with the same doses). With even the smallest filling (50 kg per cub. m) a considerably higher dose is required than for wheat. The flour evidently absorbs a great deal of gas. This is a case of a $<$ b (page 32).

The same was tried on *peas*. Each tin contained 1 kg; the dose was 30 ml per cub. m.

| Cap. tin in litres | Filling per cub. m in kg | Dose | 24 hours | 2 days |
|---|---|---|---|---|
| 10 | 100 | 0.30 | 36 | 76 |
| 5 | 200 | 0.15 | 24 | 58 |
| 3.3 | 300 | 0.10 | 22 | 66 |
| 2.5 | 400 | 0.08 | 48 | 82 |
| 2 | 500 | 0.06 | 46 | 84 |
| 1.7 | 600 | 0.05 | 44 | 84 |
| 1.4 | 700 | 0.04 | 68 | 94 |
| 10 | 100 | 0.30 | 6 | 42 |
| 5 | 200 | 0.15 | 10 | 54 |
| 3.3 | 300 | 0.10 | 24 | 66 |
| 2.5 | 400 | 0.08 | 34 | 78 |
| 2 | 500 | 0.06 | 46 | 86 |
| 1.7 | 600 | 0.05 | 32 | 82 |
| 1.4 | 700 | 0.04 | 58 | 94 |

The tendency here is obviously in the *opposite* direction: the larger the filling, the greater the effect. a $>$ b.

Summing up we find:

1. With *peas* the average concentration is higher in a filled than in an empty space (a $>$ b);
2. With *wheat* the average concentration in a filled space is equal to that in an empty one (a $=$ b);
3. With *flour* the average concentration is lower in a filled than in an empty space (a $<$ b).

Flour consequently absorbs more gas than wheat, and this again more than peas.

It was moreover found that flour is the most sensitive as to odour and taste, wheat much less so and peas practically not at all. The test method with the series of tins is therefore also highly suitable to find out in how far odour and taste are likely to be affected. It is also more exact than the direct method of fumigation, working up of the product, and tasting it. The subjective element — tasting — has a great influence in the latter method.

It should, however, be taken into account how the products are to be used afterwards. Peas, wheat and flour are either cooked or baked. With cocoa beans it is quite different. These are probably slightly more susceptible than wheat, so the effect of fumigation is slightly lower when the filling is larger. All the same, cocoa beans can be fumigated to any desired extent, for they are *roasted*, in which process any influence of the gas is eliminated.

It seemed desirable to test the above method on a quite different object. For this purpose dried apricots were used. Being slightly more sensitive to gassing than wheat, they were expected to show a somewhat smaller effect when fumigated with the same doses in a larger filling.

The tins were filled with ½ kg apricots and gassed for six hours at 20° C. See table on page 47.

Although this series shows some irregularities (tin 2.5 litres of the first series may have been wrongly dosed), there is a pronounced tendency towards decrease in effect with increasing filling, but the decrease is by no means so great as with flour. This perfectly tallies with the fact that a change in taste is slightly sooner noticeable than with wheat, but by no means so quickly as with flour.

Dried fruit in general is one of the products that can very well resist a six hours fumigation. The dose should however be a little higher than for wheat, and slightly increase with the filling.

Finally, some trials were made on wheat in the laboratory on a larger scale to test results found above.

| Cap. tin in litres | Filling per cub. m. in kg | Dose | 24 hours | 2 days | 1 week |
|---|---|---|---|---|---|
| 10 | 50 | 0.35 | 8 | 64 | 98 |
| 5 | 100 | 0.175 | 8 | 66 | 80 |
| 3.3 | 150 | 0.12 | 6 | 58 | 92 |
| 2.5 | 200 | 0.09 | 11 | 94 | 100 |
| 2 | 250 | 0.07 | 6 | 42 | 86 |
| 1.7 | 300 | 0.06 | 6 | 34 | 70 |
| 1.4 | 350 | 0.05 | 2 | 14 | 66 |
| 10 | 50 | 0.40 | 50 | 98 | 100 |
| 5 | 100 | 0.20 | 58 | 90 | 100 |
| 3.3 | 150 | 0.135 | 55 | 84 | 99 |
| 2.5 | 200 | 0.10 | 44 | 84 | 100 |
| 2 | 250 | 0.08 | 38 | 76 | 98 |
| 1.7 | 300 | 0.07 | 48 | 90 | 100 |
| 1.4 | 350 | 0.06 | 28 | 74 | 96 |

1. A bag containing 75 kg of wheat was fumigated with a dose of 54 g per cub. m in a 345 litres gassing box for six hours at 20° C. This dose is only 20 % higher than was found to be necessary by means of the tins. A gauze bag containing 50 Calandra granaria was placed in the centre of the wheat, and removed 24 hours after fumigation. 68 % were dead. A week later all the insects were dead.

2. Two bags containing 78 and 87.5 kg of wheat were placed together in a 345 litre gassing box and fumigated with a dose of 100 g per cub. m under the same conditions as in the preceding test. All the insects had died 24 hours after fumigation.

Samples of the wheat used in these tests were ground and baked. The bread was quite normal.

## VIII. BAKING PROPERTIES

The question remains whether the baking properties are influenced by the fumigation.

To ascertain this, a large number of flour samples were fumigated in 345 litre boxes at 20° C. Time and dose were varied as follows:

| Time in hours | Dose in ml | Time in hours | Dose in ml |
|---|---|---|---|
| 24 | 50 | 3 | 100 |
| 6 | 200 | 3 | 69 |
| 6 | 100 | | |
| 6 | 50 | | |
| 6 | 25 | | |

After the fumigation the flour was aired for 24 hours by spreading it on a piece of paper on a table in a well ventilated room. It was then submitted with untreated samples to the Chemische Fabriek "Chefaro" at Rotterdam. The baking properties were found to have improved rather than deteriorated by the fumigation. This continued to be the case when the flour had been stored for some months after the fumigation.

## IX. GERMINATING POWER

Besides cereals and pulse intended for consumption, sowing-seeds also frequently have to be freed from insects. It is, of course, imperative that the fumigation should not deteriorate their germinating power. Both carbon disulphide and ethene oxide are known to have a highly detrimental effect on this.

I made extensive experiments in this direction with methallyl chloride. To judge the germinating power, the fumigated seeds were sown in boxes of earth, which were embedded in the soil of a glasshouse. This gives a better judgment than with Petri dishes in the laboratory. Seeds that seem to germinate well in Petri dishes may quite possibly lack the strength to force the germ through the earth. This would lead to an altogether erroneous conclusion.

The seeds were fumigated in 80 litre boxes with a dose corresponding to 125 g per cub. m, for 24 hours at 18° C.

The results were as follows:

| Species | Number of seeds | Percentage Germinated | |
|---|---|---|---|
| | | Not fumigated | fumigated |
| Wheat | 100 | 97 | 90 |
| Rye | 100 | 75 | 72 |
| Oats | 100 | 91 | 93 |
| Buckwheat | 100 | 25 | 28 |
| Caraway | 100 | 75 | 74 |
| Cole seed | 100 | 79 | 82 |
| Vetch | 100 | 96 | 97 |
| Mawseed | 100 | 86 | 87 |
| Mustard seed | 100 | 95 | 88 |
| Lettuce seed | 100 | 35 | 32 |
| Grass seed | 100 | 65 | 65 |
| Canary seed | 100 | 96 | 92 |
| Sunflower seed | 50 | 96 | 96 |
| Peas | 100 | 92 | 91 |
| Grey peas | 50 | 92 | 96 |
| Yellow peas | 50 | 90 | 92 |
| White beans | 50 | 86 | 92 |
| Broad beans | 50 | 100 | 100 |

These figures show that the influence of the gas is different on different seeds. It is absent, or at most slight, in the majority of cases. Pulse is slightly stimulated. With wheat, mustard and canary seed there is a deterioration, but this is not serious, especially when the excessive dose is considered. Yet damage is possible when very damp seeds are fumigated. Peas stored for 24 hours in an atmosphere saturated with water vapour were found to have seriously deteriorated in germinating power.

*Other parts of plants.*

Bulbs of narcissus and tubers of dahlia and begonia were treated with a dose of 19 g per cub. m for 24 hours. They were not damaged.

Dug-out plants of delphinium (photograph 5) and chrysanthemum, subjected to the same treatment; the latter were slightly damaged.

Flowers of double and single roses and of marigolds were fumigated with a dose of 45 g per cub. m for 3 hours. The single roses were damaged.

Aphids, ants, larvae of hover-flies (Syrphides) and a spider were killed by this fumigation.

In general it may be said that inert parts of the plant are not damaged, and that growing parts are damaged in some cases.

## X. INFLUENCE OF THE FUMIGATION ON THE MARKETABILITY OF THE PRODUCT

It is conceivable that, though the quality of a product is not influenced by fumigation in an unfavourable sense, its marketability might be diminished. The colour might become different, it might acquire some offensive odour, or a similar blemish. So far, nothing of the kind has been noticed after fumigation with M, with the exception that shelled walnuts had become a little darker. No other deviation of any nature has ever been found.

The general laboratory tests were terminated herewith, and fumigation trials in practice were started.

## CHAPTER III

## FUMIGATION TRIALS IN PRACTICE

After it had been found in the laboratory tests described above that methallylchloride possesses satisfactory properties as gassing insecticide, it was decided to test this material in practice. In order to get a reliable insight into its effect, I chose test objects varying widely in nature.

The fumigation trials were not restricted to cereals and Calandra species, though standardized Calandra granaria from laboratory cultures were in most cases utilized for judging the effect.

The following tests were made:

### I. TEST IN A GASSING ROOM OF 70 CUB. M.

This room is specially equipped for fumigations with HCN. It contained the following goods:

13 bags of maize, about 1000 kg, heavily infested with Calandra oryzae L.

5 „ „ wheat, about 400 kg, affected by Calandra granaria L. and Calandra oryzae L.

2 „ „ cocoa beans, about 100 kg, affected by Sitodrepa panicea L. (drug store beetle) and by Ephestia elutella Hb. (cocoa moth).

2 „ „ peas, about 200 kg, affected by Endrosis lacteëlla Schiff.

2 „ „ apricot stones and two cases of currants, affected by Paralispa gularis Rag.

1 bag of potatoes, infested with Phthorimaea operculella Zell.
6 bags of cow-hair, affected by Dermestes lardarius L. (larder beetle).

For checking purposes I put down a number of gauze boxes containing wheat infested with Calandra granaria. One of these boxes was placed in each of the four corners on the floor, one in the middle of the floor and one in the middle half way up. One box was fixed to the ceiling, but dropped during the fumigation.

The total quantity of M used was 5 kg, which amounts to about 70 g per cub. m.

The liquid was poured out into four shallow zinc trays of about 1.25 × 0.50 m. The temperature was registered with a thermograph. It averaged 20° C. Twenty four hours after the liquid had been poured out, the exhauster was started and allowed to run for 48 hours. Any smell was absent by the end of this time. All the insects were found to be dead, and no new ones could be bred from the samples taken. The goods had evidently been cleared of all stages.

The wheat and the apricot stones had acquired a slightly musty smell (this fumigation was carried out before the investigation into the influence on smell and teste had been terminated).

The cocoa beans were sent to a chocolate works, where they were manufactured to chocolate. The quality had in no way been impaired.

## II. FUMIGATION OF A LOFT IN A COCOA FACTORY

This loft contained thousands of larvae of the cocoa moth (Ephestia elutella Hb.). Most of them had crept into the crevices of the ceiling, where they abounded in layers. The loft had two windows and three doors. There were only two bags of cocoa beans and about 400 empty gunny bags. The space had a capacity of about 150 cub. m.

All the openings were sealed off with gummed paper. In different places gauze boxes containing adults of Calandra granaria were put down. The liquid was poured into the same trays as used in the previous test. Three were placed half way up, one on the floor.

The total quantity of liquid poured out was 10 kg, which is almost 67 g per cub. m. The fumigation was started on a Saturday morning at eleven and terminated on Monday morning at nine o'clock. Scarcely any smell of gas had been noticed in the adjoining rooms during that time. To degas the loft, doors and windows were opened, so that almost all the gas had disappeared within twenty minutes on account of the strong draught. The floor was thickly covered with dead larvae, with a few convulsive specimens among them. The Calandra in the boxes — about 5000 in all — were all dead.

Two days afterwards I inspected the loft once more. All the larvae were dead now, with the exception of some live ones in the crevices of the windows. They had been covered by the gummed paper, so that the gas had not reached them or only insufficiently.

The gassing temperature was 14—15° C, hence comparatively low. This test shows that a space not specially adapted for gassing can quite well be fumigated with M without any trouble from gas being experienced in the adjacent rooms.

It is also clear from this test that larvae lodged in the crevices of the ceiling — hence high up in the room — are killed.

## III. FUMIGATION OF SOME COMPLEXES IN A COCOA WORKS

This test was on a much larger scale than the two preceding ones.

The complex consisted of eleven rooms in two buildings. They were seriously infested with Ephestia elutella.

The gassing was carried out in two operations:
a. Building with ten rooms, total capacity 2801 cub. m.
The rooms were distributed as follows:

| | | | | |
|---|---|---|---|---|
| 3rd floor | 1 | | 2 | sorting loft |
| 2nd floor | 5 | | 4 | 3 |
| 1st floor | passage | room in which beans are crushed | landing | paper loft |

The building had three storeys; on the ground floor there were offices, a passage and some unused rooms. The capacity of the rooms was as follows:

| | | | | | |
|---|---|---|---|---|---|
| Sorting loft | 420 | cub. m. | fumigated | with | 32 kg |
| Loft 1 | 420½ | ” | ” | ” | 32 ” |
| ” 2 | 222 | ” | ” | ” | 17 ” |
| ” 3 | 331½ | ” | ” | ” | 25 ” |
| ” 4 | 175½ | ” | ” | ” | 13 ” |
| ” 5 | 331½ | ” | ” | ” | 25 ” |
| Paper loft | 420 | ” | ” | ” | 32 ” |
| Landing | 54 | ” | ” | ” | 4 ” |
| Crushing room | 331½ | ” | ” | ” | 30 ” |
| Passage | 94½ | ” | ” | ” | 7 ” |
| In all . . . | 2801 | cub. m | | | 217 kg |

The dose was therefore about 75 g per cub. m. Only in the crushing room, which contained much woodwork, a slightly higher dose was applied. In most of the rooms cocoa beans were stored.

The building was very old, and had a great many windows and much old woodwork. It was difficult to seal off the rooms completely, for which purpose putty proved to be the most suitable.

The M was poured out into sixty trays totalling 200 sq.m., so that the liquid in each tray was about 1 cm high.

In many places gauze boxes were put down, each containing 50 Calandra granaria. The doors between the three rooms on each floor remained open during the fumigation. The floors were, however, separated from each other.

The fumigation was started between 10 and 11 on a Saturday morning and stopped at 9 on Monday morning, thus lasting for about 46 hours. The temperature was 16—17° C. Before degassing, some samples were taken by means of evacuated tubes.

An inspection after the fumigation showed that the floor was covered with thousands of dead moths. Not a single moth had survived.

Not all the liquid had evaporated, about 20 kg being left, so that the total quantity vaporized was 197 kg or more than 70 g per cub. m.

The actual concentration did not, of course, at any moment reach this calculated value of 70 g per cub. m. During the fumigation process liquid evaporated regularly, but gas was continuously lost, too. Owing to the slow evaporation a certain concentration was regularly maintained.

The degree of concentration can approximately be deduced from the mortality of the Calandra granaria put down. This was found to be as follows on page 56.

It may be concluded from the mortality of Calandra that the average concentration on the two top floors was about 15 g per cub. m and on the first floor 11 to 12 g per cub. m.

The risks of losses were much greater on the first floor, where paper was stored and which contained much woodwork, both of which absorb much gas. However, as Calandra granaria is much more resistant than Ephestia elutella, it is improbable that any of the Ephestia survived the fumigation.

| Space | Place where the gauze boxes were put down | Height of this place in relation to total height | Percent killed | | Percentage of gas in the air samples taken |
|---|---|---|---|---|---|
| | | | 24 h. | 1 w. | |
| Sorting Loft | On sieve. | ½ | 92 | 100 | 5.8 duplo 5.9 |
| | In heap of beans on a table near the window. | ¼ | 92 | 100 | |
| | In a pile of gunny bags. | ¼ | 57 | 100 | |
| | In a heap of waste material. | 0 | 96 | 100 | |
| Loft 1 | In fan. | ¼ | 98 | 100 | |
| | On sieve. | ¾ | 84 | 100 | |
| Loft 2 | On staircase near ceiling. | 1 | 76 | 100 | |
| Loft 3 | In a pile of bags. | ½ | 100 | 100 | |
| | Near window. | ¼ | 100 | 100 | |
| | In a bag of beans. | ¼ | 100 | 100 | |
| | In a heap of waste material. | 0 | 100 | 100 | |
| Loft 4 | In window sill. | ¼ | 88 | 100 | |
| | In sieve. | ½ | 95 | 100 | |
| Paper Loft | Near the window. | ¼ | 46 | 92 | On floor 6.2 |
| | On paper. | ¾ | 23 | 98 | Near ceiling |
| | On a beam. | 1 | 4 | 75 | 6.8 duplo 8.0 |
| Landing | In a corner | 0 | 8 | 86 | |
| | Ditto. | 0 | 14 | 88 | |
| Breaking space | On a beam. | ¾ | 4 | 52 | On floor 11.2 |
| | In a cupboard with waste material. | 0 | 66 | 100 | Near ceiling |
| | Near the window. | ¼ | 17 | 83 | 5.6 |

A remarkable result was obtained on the paper loft, where gauze boxes were placed at three different heights.

| Height | Killed after | |
|---|---|---|
| | 24 hours | 1 week |
| ¼ | 46 | 92 |
| ¾ | 23 | 98 |
| 1 | 4 | 75 |

It would seem from these figures that the concentration was lower at the top of the loft, so that the gas must have sunk down to some extent.

b. Building with a capacity of 1300 cub. m, consisting of one room for crushing beans. There was a lot of woodwork, so that the sealing was very difficult. A driving shaft ran through a wall to another room. The hole around this shaft was closed by stuffing it with jute sacking. In addition, boards, putty and gummed paper were used for sealing off.

There was much cocoa powder on the walls of the conveyors in the room, which also contained a large number of bags of cocoa beans. For checking purposes eight boxes, each with 50 Calandra granaria, were placed on various spots.

The dose applied was 90 g per cub. m. The liquid was again poured out into trays.

By way of trial woollen flannel cloths were hung over two troughs, so that they hung down one metre on all sides. Evaporation was greatly accelerated by this.

The fumigation was started between twelve and one o'clock on Saturday and finished at 8.15 on Tuesday, so that it lasted about 67 hours in all. The liquid had then completely evaporated. Fumigation temperature 18—19° C. The floor was strewn with dead moths, none had survived. All the Calandra were also dead. A quantity of cocoa powder was taken from the conveyors and placed in the laboratory incubator at 28° C.

After five months no signs of life had been noticed in this sample.

These two fumigations were carried out by the end of May. In the period from May to November moths were found only sporadically in the works; a pest as in previous years was out of the question. This proves that this factory can be kept free from moths by gassing once a year or perhaps once every other year.

## IV. FUMIGATION OF AN OLD WAREHOUSE

The building was very old and seemed at first impossible to seal off. Yet a fumigation was decided upon, which meant a very severe trial to the fumigant.

In the warehouse base materials for a confectionery were stored, which were affected by Ephestia elutella and Paralispa gularis. It had four storeys, the first of which was divided into smaller rooms (offices etc.).

In order to ascertain whether the quality of the stored products could be influenced by the gas, I fumigated samples in the laboratory. These samples consisted of the following products, 2 kg of each: almonds, apricot stones, shelled hazelnuts, grated cocoanut, shelled walnuts, sultanas, American raisins, muscatels, currants, candied peel, moist sugar, cornflour, wheat-flour, corn flakes and ginger.

All these samples were spread out on wooden grids with paper in a 345 litre gassing box. Ephestia larvae and adults of Tribolium confusum were also placed there for checking purposes.

The fumigation took place with a dose of 100 g per cub. m for 6 hours at 20° C.

The insects were immediately killed. The products were worked up to cake and pastry in the usual manner. They proved to be unaffected, the only exception being that the wheat-flour had become slightly musty in taste and that the walnuts had become a little darker.

The fumigation could, therefore, be started after the removal of the stored wheat-flour.

The building was closed off as well as possible, but this could not be done completely. The storeys could not be closed separately, so that they remained in connection with each other.

The furniture in the offices: chairs, writing tables, carpets, heavy curtains, etc., were left in the building.

As the fumigation was not allowed to last longer than six hours, the method of slow evaporation could not be applied. Instead, the liquid was atomized by means of fine atomizers and cylinders of compressed air.

The capacity of the five rooms was:

| | |
|---|---|
| Ground floor . . . . . | 264 cub. m |
| first „ . . . . . | 330 |
| 2nd „ . . . . . | 330 |
| 3rd „ . . . . . | 330 |
| loft . . . . . . . . . | 276 |
| In all . . . . . . . . . | 1530 cub. m |

The total height was about 14 m.

The quantity of liquid used was 107 kg, corresponding to 70 g per cub. m.

For checking purposes, gauze boxes were put down here and there, containing adults of Calandra granaria and larvae of Ephestia kühniella and Borkhausenia pseudospretella.

The liquid was atomized very rapidly, the whole building being filled gas within an hour. Six hours later doors and windows were opened. The top floors were free from gas within a few minutes, the lower took much longer. The gas had evidently sunk down.

All the insects were dead; on the top floor a few convulsive moths were found, which were also dead after 36 hours. All the flies and spiders had been killed as well; moreover, I found a number of Anobium species, apparently from the old beams.

A number of dead moths (Tineola biselliella Hum.) were found near the office curtains.

No damage had been done to the furniture.

The insects in the gauze boxes were inspected 40 hours after fumigation, the result being:

| | Calandra | Ephestia | Borkh. |
|---|---|---|---|
| Ground floor | 100 % | — | — |
| 1st floor | 100 % | 100 % | 100 % |
| 2nd „ | 86 % | 60/52 % | 61/30 % |
| 3rd „ | 4 % | 31 % | 38 % |
| 4th „ | 5 % | 5 % | 0 % |
| *Six days later* | | | |
| Ground floor | 100 % | — | — |
| 1st floor | 100 % | 100 % | 100 % |
| 2nd „ | 98 % | 72/72 % | 88/72 % |
| 3rd „ | 49 % | 84 % | 88 % |
| 4th „ | 7 % | 55 % | 11 % |

This clearly proves that the gas had sunk down.

When some floors in a building have to be gassed simultaneously all communication between them should therefore be prevented. In very high spaces the gas should be kept moving by fans.

## V. FUMIGATION IN A SPECIAL VACUUM INSTALLATION

By the special kindness of Mr. Barges at Le Hâvre I had an opportunity of making a series of tests in the vacuum installation of the "Station de désinfection des produits végétaux".

This installation works as follows: the goods are passed into a vacuum tank, in which pressure is reduced by about 650 mm. The liquid is drawn in by suction, passing through a coil in a hot water bath and consequently quickly evaporating. The admittance of the gas reduces the vacuum to about 200 mm, upon which the air is allowed to rush in so as to get an intimate air gas mixture. The gas consequently penetrates very rapidly into the goods.

Fumigation is terminated by twice applying vacuum and admitting air, owing to which the goods are practically freed from gas.

I will only mention here a large-scale test in a 29 cub. m tank. It contained 5000 kg of maize, seriously infested by Calandra oryzae and Tribolium spec. and a bag of wheat, seriously affected by Calandra granaria. Dose 74 g per cub. m, for 6 hours, temperature about 19° C.

After the fumigation some insects only showed slight convulsions, the majority was dead.

The batch of maize did not remain at our disposal, but we kept the wheat. Three months later not a single insect was to be found in it. A small quantity of potatoes with three larvae of the Colorado beetle (Leptinotarsa decemlineata) were gassed at the same time. The insects were killed, but the potatoes were damaged, as they could not develop to good plants.

This method of fumigation is decidedly the most satisfactory and reliable.

## VI. LARGER QUANTITIES OF SOME PRODUCTS FUMIGATED IN 345 LITRE LABORATORY GASSING BOXES

*a.* About 350 unprepared fox skins were fumigated against Dermestes lardarius.

The boxes were crammed with skins. These skins contained a good deal of grease, and a M dissolves in this, much loss was to be expected.

70 g per cub. m, applied for 24 hours, amply sufficed to kill all the insects. The fur remained absolutely unaltered. This result induced a fur dealer to construct a fumigation chamber, in which many batches of skins are now being successfully treated.

*b*. Three bales of Taschowa tobacco, each weighing about 20 kg, were obtained from a tobacco company.
One of these bales was gassed with a dose of 120 g per cub. m for 3 hours. The bales were then stored for four months. It was impossible for experts to distinguish the gassed bale from the other two, so that the quality had evidently remained absolutely unaltered.

## VII. SUMMARY OF THE TESTS MADE

1. Special gassing room, 70 cub. m.
   Dose 70 g per cub. m, time 24 hours, temp. 20° C. All the insects dead after fumigation. The dose might have been lower.
2. Loft cocoa works, 150 cub. m.
   Dose 67 g per cub. m, time 46 hours, temp. 14—15° C. All the insects dead after fumigation. Dose amply sufficient.
3. Complex cocoa works
   *a*. 2801 cub. m.
   Dose 75 g per cub. m, time 46 hours, temp. 16—17° C. After fumigation: moths dead, not all the Calandra. Dose exactly sufficient.
   *b*. 1300 cub. m.
   Dose 90 g per cub. m, time 67 hours, temp. 18—19° C. All the insects dead after fumigation. Dose sufficient.
4. Old warehouse, 1530 cub. m.
   Dose 70 g per cub. m, time 6 hours, temp. about 20° C. Gas had sunk; the dose was presumably sufficient.
5. Vacuum installation, 29 cub. m.
   Dose 74 g per cub. m, time 6 hours, temp. 19° C. All the insects dead after fumigation; dose amply sufficient.
6. *a*. Unprepared skins can be fumigated with a dose of 70 g per cub. m for 24 hours.
   *b*. The quality of the tobacco is presumably not altered by the fumigation.

## VIII. PROTECTION OF THE PERSONS CARRYING OUT THE FUMIGATION

In all the tests gas masks were used provided with eyeglasses and with canister A of the Degea. The masks permit of a prolonged stay in the rooms where the liquid is poured out, because the concentration never becomes high.

Great caution is, however, imperative when the liquid is atomized (test IV), because in this case a high concentration is rapidly attained. Some mist is then formed as well, so that the gas mask should be fitted with a mist filter. In this case Otter and Groenendijk's canister, of Belgian origin, may for instance, be used.

Anyhow it is desirable to leave the space immediately after opening the nozzles. A stay of longer than 30 minutes in the gassing space with the same canister is impossible.

All fumigations, with M as well as with other gassing insecticides, in which the gassing space has to be entered, should be carried out by more than one person: preferably two entering the room and one staying outside.

The toxicity of M for higher animals in comparison with that of other gases is discussed in Chapter IV.

## IX. IRRITATING EFFECT OF M ON THE INSECTS

It has been stated before that M has a very strong after-effect. Immediately after the gassing not all the insects are dead; they die successively, however, in the hours and days following the fumigation. For this reason the insects were observed for a week after each gassing. Even after this the after-effect is presumably not yet spent.

M has, however, another highly important property, which was noticed in the tests.

It is known that insects shield themselves from some insecticides by so-called protective stupefaction. They are rigid and hardly move or breathe. The effect of the gassing is, of course, greatly lessened by this. HCN has this influence and for this reason frequently substances are added which irritate the insects, such as various methyl esters. The drawback is that the irritating substances do not penetrate sufficiently, so that the insects are not reached. In the present experiments I found that M itself possesses strongly irritating properties. Even a low concentration causes the insects to become greatly disturbed and to emerge from their hiding places.

In trial II, on the cocoa loft, thousands of larvae were lodged in the crevices of the ceiling. They had already started spinning their cocoons, one clinging to the other, thus forming a cluster of many layers. At the end of the fumigation it was found that nearly all of them had come out and dropped to the floor.

In fumigating the cocoa works it was observed through the windows that the moths, which had at first kept quiet in their hiding places, began to flutter about wildly as soon as the gas was introduced.

Upon gassing of some pieces of furniture numerous larvae and adults of Anobium species appeared. Larvae of Sitodrepa panicea emerged when cattle cakes were treated.

M consequently proves at the same time to possess insecticidal and irritating properties.

This may be of great importance for instance in the case of dwelling fumigation. The bugs, which mostly hide in inaccessible places, will also be roused up and thus are sure to be reached by the gas.

## X. CONCLUSIONS AND FURTHER DATA FROM THE ABOVE TRIALS

*Fumigation time of 24 hours and longer.*

This can be applied in buildings that are fumigated in the weekend and in sheds where goods are stored whose smell or taste is unaffected by the gas, such as cocoa beans and goods that are not consumed, such as skins.

With a fumigation time of 24 hours the *actual* concentration must be about 20 g per cub. m; with a time of 40 hours and more, about 12 to 15 g per cub. m.

The dose entirely depends on the circumstances. In specially constructed gassing chambers and vacuum installations a dose of 30—40 g per cub. m will in most cases be found to suffice.

For products such as skins, the hairs of which absorb a large quantity of gas which, moreover, dissolves in the grease, a substantially higher dose — about 70 g per cub. m — is required.

In buildings containing a great deal of woodwork or which cannot be completely sealed off the dose should also be higher. It should be adopted to the prevailing conditions.

In most cases by far 75—90 g per cub. m will be sufficient.

When there is a great risk of losses, it is advisable to evaporate the liquid slowly by pouring it out to a height of 1 cm in flat trays. This provides a constant supply of gas; the concentration consequently is not very high, the losses are less great and are constantly replaced.

The troughs should be placed as high up as possible. If necessary, evaporation can be accelerated by hanging cloths of woollen flannel in the trays and over the edges, which should then not be higher than 4 cm.

Before the fumigation the space should be closed off as well as possible. Gummed paper, thin wood or putty can be used for this purpose. Large holes can be stuffed with moist gunny bags.

When fumigation has been started, thorough inspection should be made on the outside to ascertain whether any gas escapes, which is at once noticeable from the smell.

The person entering the room to degas it should wear a gas mask and open all the doors and windows.

*Fumigation time of* 8 *hours or less.*

For many products it is advisable to choose a short fumigation time — say of 8 hours — so as to prevent any disagreeable effect on odour or taste. A dose of about 65 g per cub. m suffices when the fumigation space is thoroughly sealed off. In cases where losses are to be feared the dose should be increased accordingly.

The best way of supplying the gas is by atomizing it finely; in vacuum installations the liquid can be conducted through a heated coil. For the atomization low-pressure steel cylinders can be used, filled with liquid and air to about 20 atm. (photograph 7).

*Gram-hour value.*

In calculating the dose use can be made of the gram-hour value, i.e. the number of grams applied per cub. m. multiplied by the time (see also the next chapter). Under practical conditions this is about 500—1000 for M. With a fumigation time of six hours in a well-closed installation the dose is about 500 : 6 = approximately 80 g per cub. m; with a fumigation time of eight hours 500 : 8 = approximately 60 g per cub. m. The gram-hour value rises greatly when much absorbent material or many other factors causing loss are present and *when the time of fumigation is much longer*. For a fumigation time of 24 hours, 20 g per cub. m is not sufficient, but should be about 40 g per cub. m, which corresponds to 960 gram-hours. This has been worked out in Chapter IV.

For further directions for use see page 92.

# CHAPTER IV

# CONTINUED LABORATORY INVESTIGATIONS

## I. INTRODUCTION

Both in the general laboratory investigation and in the practical experiments it was found that methallyl chloride is very valuable for the control of noxious insects.

During the investigation, however, a number of questions partially of practical and partially of theoretical importance remained open.

At this moment, however, it is not possible to furnish a complete explanation for all questions which arise during the use of M. As far as possible I will give a number of preliminary conclusions, while further information will be supplied in following publications.

## II. PROPORTION OF CONCENTRATION TO TIME. GRAM-HOUR VALUE

The first question which arises is: "Does methallyl chloride provide any advantages over other known insecticides and if so, why?"

Peters (34) denies these advantages in an paper which may be regarded as a reply to my short note in Nature (25).

He apparently judges the value of a gas insecticide entirely by figures obtained in the laboratory. It is regrettable that he omitted to mention in what manner and in how many experiments these figures were obtained. For that reason his conclusion that methallyl chloride compares very unfavourably with ethene oxide and even with carbon disulphide is by no means convincing.

Peters regards the „Grammstundeneinheit" (gram-hour unit) as the most important value. It is clear that if the *fumigation period* is shortened, the *concentration* should be increased. According to many authors this is directly proportional, c × t therefore is a constant value (Haber's law).

Already in 1936 Peters (30) suggested expressing the value of a gas in "gram-hour" units. The smaller the activity of the gas, the more "gram-hour" units will be required to obtain a good effect. Later Peters stated (35) that this only applies to HCN and not to other gases.

This matter I closely investigated under various conditions with respect to M.

To this end fumigations were first carried out in gassing boxes with a capacity of 80 litres. Fifty Tribolium confusum Duv. were placed in each gassing box and fumigated for different periods.

For this series of experiments the following results were obtained:

| Fumigation time | Dose per box in ml. | Per cent killed in | |
|---|---|---|---|
| | | 24 hours | 1 week |
| 3 hours | 6 | 16 | 78 |
| 3 „ | 6.5 | 14 | 84 |
| 3 „ | 7.0 | 42 | 98 |
| 6 „ | 3.5 | 22 | 100 |
| 6 „ | 4.0 | 46 | 100 |
| 6 „ | 4.5 | 40 | 100 |
| 24 „ | 1.5 | 66 | 96 |
| 24 „ | 1.6 | 60 | 100 |
| 24 „ | 1.7 | 80 | 100 |
| Blank I | | 0 | 0 |
| „ II | | 4 | 4 |

The following values may be derived from this series:

Fumigation time 24 hours, dose about 1.5 ml
" " 6 " " less than 3.5 ml
" " 3 " " about 7.0 ml

This shows that for a fumigation time of 24 hours about 1.5 ml is required and for 3 hours about 7 ml. It should be taken into account that the time required to evaporate 7 ml of M is fairly long as compared to the entire fumigation time of 3 hours.

I attempted to obviate this difficulty by the following procedure. A fan was placed in a 345 litres gassing box described elsewhere. A small pump with a capacity of about 4 litres per min. was connected to the gassing box. This pump removed the gas from the box, caused it to pass through three wash bottles (without liquid) and back to the gassing box.

At the beginning of the experiment the tube leading to the pump was closed. The gassing box was also closed and the required quantity of liquid was introduced through the aperture at the top. Then the fan was switched on and kept running during the experiment. After the liquid had evaporated completely, a gauze bag containing 50 Tribolium was placed in each of the three wash bottles.

Then the tube leading to the pump was opened and the latter set going. At this moment the fumigation actually started. Fumigation was carried out for three hours and for six hours.

The following results were obtained in the first series:

| Fumigation time | Dose per cub. m in ml | 24 hours | 1 week |
|---|---|---|---|
| 3 hours . . . . . . . . . . . . | 69.6 | 48 | 98 |
| Duplicate . . . . . . . . . . . | | 32 | 84 |
| Triplicate . . . . . . . . . . . | | 40 | 88 |
| 3 hours . . . . . . . . . . . . | 69.6 | 46 | 100 |
| Duplicate . . . . . . . . . . . | | 20 | 100 |
| Triplicate . . . . . . . . . . . | | 20 | 98 |

| Fumigation time | Dose per cub. m in ml | 24 hours | 1 week |
|---|---|---|---|
| 6 hours . . . . . . . . . . . . | 40.6 | 36 | 98 |
| Duplicate . . . . . . . . . . . | | 46 | 100 |
| Triplicate . . . . . . . . . . . | | 52 | 98 |
| 6 hours . . . . . . . . . . . . | 40.6 | 20 | 98 |
| Duplicate . . . . . . . . . . . | | 32 | 96 |
| Triplicate . . . . . . . . . . . | | 20 | 98 |
| Average 3 hours . . . . . . . . | | 34 | 95 |
| Average 6 hours . . . . . . . . | | 34 | 98 |

Using the value for a fumigation period of 24 hours obtained in the previous series, the following rough values are obtained:

| Fumigation period in hours | Dose cub. m. in ml | Dose cub. m. in g | 24 hours | 1 week |
|---|---|---|---|---|
| 24 | 18.75 | 17.34 | 66 | 96 |
| 6 | 40.6 | 37.56 | 34 | 98 |
| 3 | 69.6 | 64.38 | 34 | 95 |

Roughly the gram-hour values under the conditions described are:

for 24 hours 416
,, 6 ,, 225
,, 3 ,, 193

A remarkable thing is that with higher concentrations and therefore with a shorter period of activity the gram-hour values are *lower*.

Here the values for 24 hours, 6 hours and 3 hours are related in a proportion to each other of about 2.15 : 1.17 : 1.

The following values (for Calandra granaria) were found on fumigation of 2 kg of wheat in glass jars of 3.1 litres:

| Fumigation period | Dose per kg in ml | Dose per cub. m in ml | Dose per cub. m in gram | gram-hours |
|---|---|---|---|---|
| 24 | 0.045 | 28.8 | 26.64 | 639 |
| 6 | 0.095 | 61.0 | 56.43 | 338 |
| 3 | 0.160 | 103.0 | 95.28 | 286 |

Proportion = 2.24 : 1.18 : 1.

Here the gram-hour values are higher, because the gas had to penetrate through a layer of wheat. The *proportion*, however, is practically equal to that in the gassing boxes.

There is an indication here that the gram-hour value indeed decreases as the concentration becomes higher. In that case the gas has a better effect in higher concentrations and with shorter fumigation periods than in lower concentrations.

However, these are only rough experiments; in order to obtain more accurate results they should be worked out in detail.

The most important objections which may be raised are:

1. If a liquid is evaporated in a space where atmospheric pressure prevails, a slight excess of pressure is the result. In the wooden boxes this will cause a loss of gas owing to the mixture partly escaping.
2. The liquid takes sometime to evaporate, as a result of which the time during which the gas is effective cannot be determined accurately.
3. The adsorption to the walls is considerable.
4. The concentration in the boxes will not be completely homogeneous.

In view of this criticism apparatus had to be constructed meeting the following requirements.

1. The evaporation of the liquid may not cause excess of pressure. This may be obtained by evaporating it in a space where part of the air has previously been removed (vacuum).
2. The insects may only be placed in the apparatus after all the liquid has evaporated.

3. The apparatus should be made of a material which adsorbs only very little gas.
4. The gas-air mixtures should be continuously kept in motion.

To meet these requirements I constructed an apparatus as shown in fig. 2.

*C* and *d* are glass bottles each with a capacity of 10 litres. These bottles are connected at the top by means of a glass tube. A wash bottle *b* is connected to bottle *c*; *b* is connected to the pump *f* by means of a tube, the other end of which is connected to a series of wash bottles 1 to 5 and also to the glass tube *e*. The other end of this conglomerate is connected to the bottom of bottle *d*.

Bottles 1 to 5 are glass wash bottles with a capacity of 20 ml, provided with a double-pierced, ground-in glass cover.

Pump *f* is a tube-pump, which consists of a length of rubber tubing tightly stretched round three cams fixed to a rotating disk. The capacity of this pump is about 4 litres per minute.

A duplicate of the apparatus is built symmetrically to the described one. The four bottles are placed in a water bath. The two pumps are driven by the same motor. The whole apparatus is placed in a room with a constant temperature of 20° C.

The procedure is as follows:

The wash bottle *b* is removed and the resulting break in the apparatus is connected up. The three-way cocks I to VI are adjusted so that bottles 1 to 5 are turned off and tube *e* is open.

A vacuum pump is then connected to the three-way cock *a*. This pump reduces the pressure in the bottles *c* and *d* to about 10 mm Hg. The liquid required is introduced into the wash bottle *b*, which is removed. As soon as the required vacuum is obtained this wash bottle is again inserted in the system. Air is then allowed to enter through the cock *a*, via the wash bottle. The liquid evaporates and this vapour is forced into the bottles by the current of air. Care must be taken that all liquid is evaporated before atmospheric pressure in the bottle is restored. Then cock *a* is closed and the pump is started. The

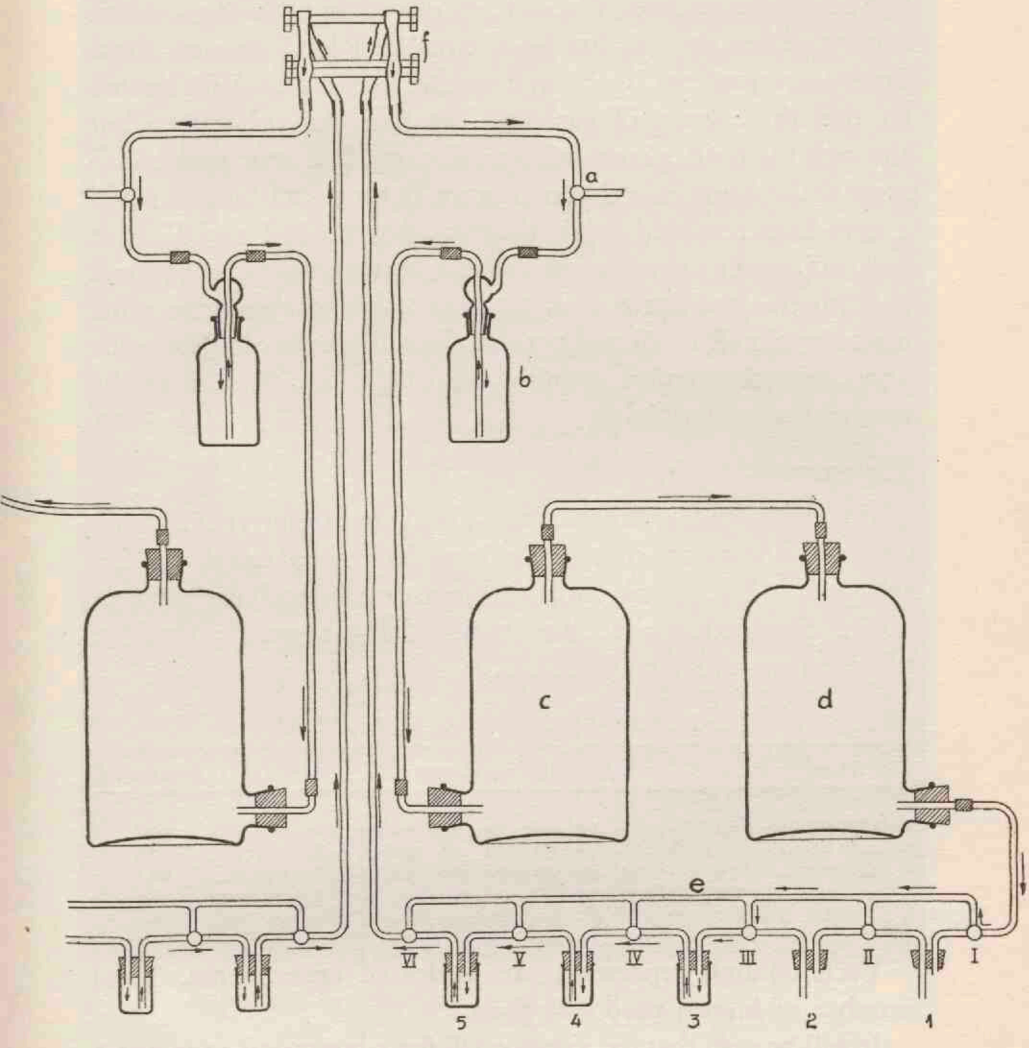



Fig. 2

gas-air mixture is circulated for about one hour to make it homogeneous.

Meanwhile 50 insects have been placed in each of the wash bottles. After the gas has been circulated long enough these bottles are inserted in the system and cocks I to VI adjusted so that the current of gas does not pass through tube *e* but through the bottles containing the insects. It is now possible to remove these bottles at different times. In the sketch bottles 1 and 2 have been removed, while the three-way cocks I and II have been adjusted so that the gas reaches bottle 3 via part of tube *e*.

With this apparatus it is made possible to apply the same concentration for different periods. So it is possible to determine accurately the period required to obtain 100 % kill at the concentration applied.

*Experiments.*

For the following experiments I always used adults of Calandra granaria, one month old. The kill was determined one week after fumigation. Each bottle contained 50 insects for each experiment.

The fumigation time was varied for the same dose. The temperature was always 20° C.

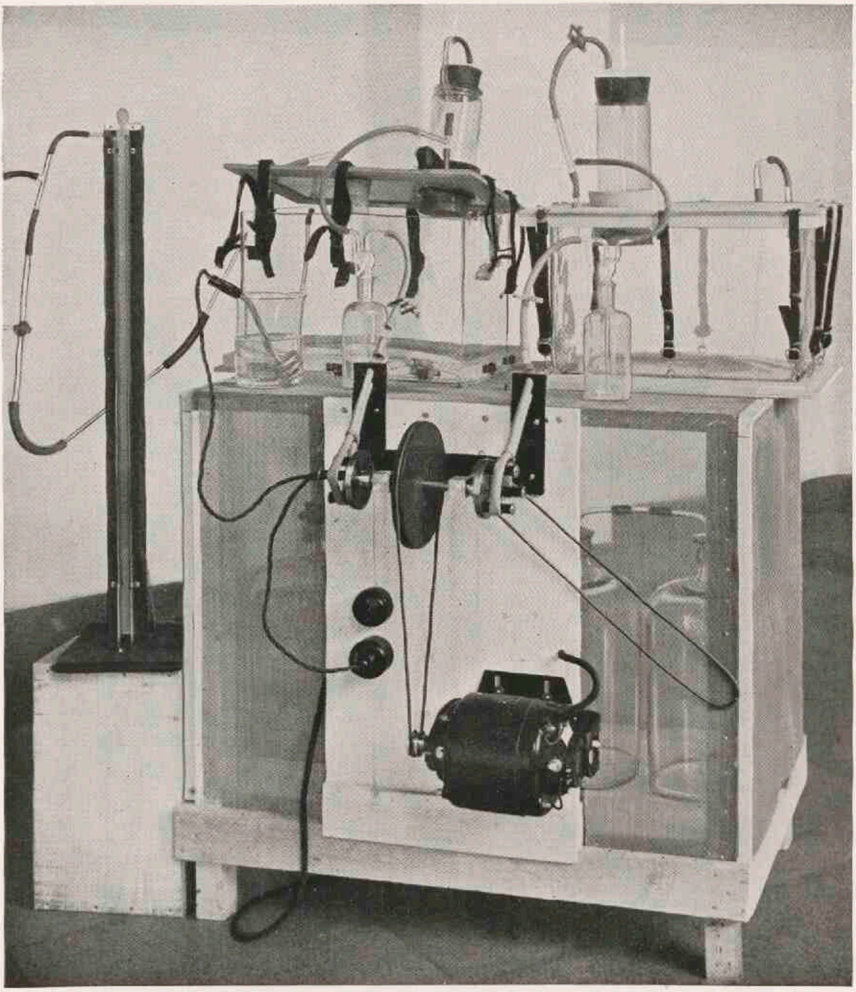
I. DOSE 65 ML = 60.1 G PER CUB. M

| Time | Kill in per cent | | | | | | | | | | | | Average kill |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2 hours 40 min. | 94 | 98 | 82 | 94 | 90 | 96 | 98 | 94 | 94 | 90 | 96 | 90 | 94.7 |
| 2 „ 50 „ | 98 | 98 | 88 | 96 | 92 | 100 | 98 | 98 | 96 | 96 | 100 | 96 | 96.3 |
| 3 „ — „ | 96 | 100 | 94 | 96 | 92 | 94 | 100 | 98 | 94 | 98 | 98 | 98 | 96.5 |
| 3 „ 10 „ | 100 | 100 | 100 | 100 | 88 | 94 | 100 | 100 | 96 | 98 | 100 | 100 | 98.0 |
| 3 „ 20 „ | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 94 | 100 | 100 | 100 | 99.5 |

Each column represents one series of experiments. Total number of insects used was 3000.

It will be seen that the average kill for 3 hours and 20 minutes is 99.5 %, while this is 100 % in 11 out of the 12 series.

The "gram-hours" value must therefore be somewhat, but only a little, higher than $3\frac{1}{3} \times 60.1 = 200$. This experiment was repeated with a somewhat higher dose.



6. Apparatus for fumigation of rats. Compare fig. 3

7. Cylinder for atomizing M liquid

II. DOSE 70 ML = 64.8 G PER CUB. M.

| Time | Kill in per cent | | | | | | | | | | | | | | | | | | | | Average |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2 h. 40 min. | 95 | 94 | 94 | 95 | 94 | 90 | 98 | 90 | 98 | 96 | 98 | 98 | 84 | 94 | 100 | 100 | 100 | 98 | 98 | 100 | 95.7 |
| 2 „ 50 „ | 98 | 100 | 94 | 96 | 96 | 100 | 94 | 92 | 100 | 98 | 100 | 100 | 92 | 100 | 100 | 100 | 96 | 98 | 100 | 100 | 97.7 |
| 3 „ — „ | 98 | 100 | 100 | 98 | 98 | 98 | 100 | 100 | 98 | 96 | 100 | 100 | 94 | 96 | 100 | 100 | 100 | 100 | 98 | 100 | 98.7 |
| 3 „ 10 „ | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 96 | 96 | 100 | 100 | 100 | 98 | 100 | 100 | 98 | 100 | 100 | 100 | 99.4 |
| 3 „ 20 „ | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 109 | 100 | 100 | 100 | 100 |

Total number of insects used was about 5000.

In this case a kill of 99.4 % was obtained with a fumigation time of 3 hours and 10 minutes, while with a fumigation time of 3 hours and 20 minutes all the insects were killed.

The gram-hour value therefore lies between 205 and 217. This result corresponds very well with that of the previous series of experiments.

I also carried out a number of other experiments with different fumigation times.

III. FUMIGATION PERIOD 1 HOUR. DOSE 165 G PER CUB. M.

| Time | Kill in per cent | | | | | | | | | | | | | | | Average |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 h. 50 min. | 98 | 98 | 98 | 94 | 98 | 98 | 96 | 98 | 90 | 88 | 98 | 94 | 88 | 100 | 92 | 95.2 |
| 0 „ 55 „ | 100 | 96 | 100 | 100 | 100 | 100 | 98 | 98 | 86 | 98 | 98 | 98 | 94 | 94 | 96 | 97.1 |
| 1 „ — „ | 100 | 100 | 98 | 100 | 100 | 100 | 100 | 100 | 96 | 100 | 96 | 98 | 98 | 92 | 100 | 98.5 |
| 1 „ 5 „ | 98 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 96 | 98 | 98 | 98 | 96 | 94 | 98 | 98.4 |
| 1 „ 10 „ | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 96 | 100 | 100 | 100 | 100 | 100 | 100 | 99.7 |

Total number of insects used was about 3750.

A kill of 99.7 % was therefore obtained after a fumigation period of 1 hour and 10 minutes. The gram-hour value therefore lies somewhat higher than $1^1/_6 \times 165 = 193$.

IV. FUMIGATION TIME 2 HOURS. DOSE 92.5 G PER CUB. M

| Time | Kill in per cent | | | | | | | | | Average |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 hour 40 min. | 98 | 94 | 90 | 92 | 96 | 92 | 96 | 90 | 98 | 94.0 |
| 1 „ 50 „ | 96 | 100 | 94 | 98 | 98 | 100 | 100 | 96 | 100 | 98.0 |
| 2 hours — „ | 100 | 98 | 98 | 100 | 100 | 100 | 100 | 96 | 100 | 99.1 |
| 2 „ 10 „ | 100 | 100 | 96 | 100 | 100 | 100 | 100 | 100 | 100 | 99.6 |
| 2 „ 20 „ | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |

Total number of insects used was about 2250. A kill of 99.6 % was obtained with a fumigation period of 2 hours and 10 minutes and a kill of 100 % after 2 hours and 20 minutes.

The gram-hour value therefore lies between 200 and 216.

V. FUMIGATION TIME 4 HOURS. DOSE 52.5 G PER CUB. M

| Time | Kill in per cent | | | | | | | | | | | | Average |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 3 hours 20 min. | 92 | 96 | 88 | 92 | 94 | 96 | 98 | 98 | 100 | 94 | 98 | 98 | 95.3 |
| 3 ,, 40 ,, | 96 | 98 | 96 | 100 | 100 | 96 | 100 | 98 | 100 | 98 | 100 | 94 | 98.2 |
| 4 ,, — ,, | 98 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 99.8 |
| 4 ,, 20 ,, | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| 4 ,, 40 ,, | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |

Total number of insects used was about 3000. The kill is 99.8 % with a fumigation time of 4 hours, so that the gram-hour value lies somewhat higher than 210.

Summarizing, we obtain the following figures:

| Fumigation time | Dose | Gram-hours |
|---|---|---|
| 1 hour 10 min. | 165 g/m³ | ca. 193 |
| 2 ,, 10 ,, | 92.5 ,, | ,, 200 |
| 3 hours 20 ,, | 60.1 ,, | ,, 200 |
| 4 ,, — | 52.5 ,, | ,, 210 |

The gram-hour value of methallyl chloride, therefore, is about 200, while moreover it is possible that this value becomes slightly higher if the fumigation time is longer.

Let us realize here exactly what is represented by the gram-hour value. This is the figure obtained by multiplying the number of grams of fumigant which are *supplied* per cub. m. by the number of hours for which the insects must be exposed to obtain 100 % kill.

It will be evident that this *gram-hour value* is quite different from the *Haber value*, which is obtained by multiplying the number of milligrams per litre of *actual concentration* by the number of minutes of the fumigation period. One is only allowed to compute the Haber value by simple multiplication if the concentration remains constant during the entire fumigation period. The Haber value may also be expressed in grams per cub. m. and hours. I should like to refer to this figure as the c.t value. This c.t value will always be lower than the gram-hour value, because of the latter including the over dose needed to compensate for losses by sorption and leakage.

According to Haber this c.t figure amounts to a constant value for a certain percentage of kill ($c \times t = K$).

The gram-hour value, on the contrary, depends upon the circumstances under which the fumigant is applied. The more favourable these circumstances, i.e. the fewer the losses, the more the gram-hour value will approximate the c.t value.

In order to obtain some idea of the extent of the losses in my apparatus (by sorption to the walls of the containers), I took samples of the gas after the apparatus had been filled with 70 ml of M per cub. m or 64.7 g. An average of 51 g per cub. m was determined in these samples of gas. The loss therefore was 13.7 g or about 21 % of the dose.

A number of measurements were furthermore carried out with a similar apparatus, dosed with 100 g per cub. m. In this case the partial pressure of methallyl chloride is equal to 27 cm of water pressure. With the aid of a water manometer it was observed that after 2 hours the pressure drop was about 6.5 cm and after three hours about 7.5 cm. This corresponds to a loss in concentration of M of 24 % to 28 %.

These two determinations show that the loss in concentration is roughly 20 to 25 %, so that the actual concentration is about 75 to 80 % of the dose.

The "approximated c.t value" of M for Calandra granaria is therefore 75 to 80 % of 200 or 150 to 160, for a kill of 100 %.

I also carried out a number of tentative determinations with carbon disulphide in the same apparatus. The dose was 100 g per cub. m.

| Time | Kill in per cent (after 1 week) | | | |
|---|---|---|---|---|
| 3 hours — min. | 76 | 90 | 70 | 74 |
| 3 ,, 30 ,, | 99 | 100 | 88 | 90 |
| 4 ,, — ,, | 100 | 99 | 99 | 100 |
| 4 ,, 30 ,, | 99 | 100 | 99 | 100 |
| 5 ,, — ,, | 100 | 99 | 100 | 100 |

This shows that the kill is satisfactory only after a fumigation period of four hours, whereas even after five hours the kill obtained is not definitely 100 % yet. The gram-hour value of carbon disulphide for Calandra granaria, determined in this apparatus therefore lies in the order of magnitude of 400.

For methallyl chloride Peters (34) gives about 275 and for carbon disulphide about 195, as may be read from his graphs. It is not evident, however, whether these figures represent gram-hour values or approximated c.t values. In any case the proportion of M to $CS_2$ as 275 : 195 is decidedly incorrect. I feel almost sure of the cause of this incorrectness. The *after effect* of M is very strong, while carbon disulphide, on the other hand, shows a strong *knock-down* effect, but the insects revive again. Probably Peters did not keep the insects under observation long enough.

It is striking how very little information regarding the insects used is supplied by non-biologists carrying out experiments upon insects. What age were the insects used? Were they standardized? At what temperature were they kept?

In a paper by Peters and Ganter (36) they state that, for their experiments, they used Calandra granaria "from the same culture, of the same size, of the same colour (tiefschwarz), of the same feeding condition and of the same temper (measured by their intensity of motion)"! — In my opinion these are not the essential facts for the choice of one's tests insects. Besides, the number of insects which these authors use in one trial — mostly ten — must be considered insufficient.

The value of many, otherwise excellent, publications is decreased by the fact that in many cases incorrect criteria are taken into account as regards the test objects! —

We now have the disposal of the approximated c × t value of M, which is about 160.

For ethene oxide Peters gives about 60. But may this be regarded as proof that the latter is a much stronger gaseous insecticide than the former?

Here now the difference between gram-hour value and c.t value becomes evident. The latter value is an entirely theoretical one, which only can be determined approximately in laboratory trials. An insecticide, however, is intended to be used in *practice*.

The dose of ethene oxide which is used *in actual practice* is 50 g for 20 to 24 hours, which corresponds to 1000 to 1200 gram-hours. This figure is out of all proportion to the value of 60 gram-hours found in the laboratory. The losses caused by adsorption and other factors are about 20 times as much as this value. The *practical* value can only be determined by *using* the material under varying conditions in *actual practice* or under conditions which are nearest to those prevailing in actual practice. This leads us to a second shortcoming of many publications on gaseous insecticides, viz. *their lack of practical examples*. The final evaluation is only possible in actual practice, laboratory experiments can only be regarded as tentative. Now we shall compare trials in actual practice with M with the prescribed practical dose of ethene oxide. In experiment V (page 60) carried out in the vacuum apparatus the dose was 74 g per cub. m for six hours, which corresponds to 444 gram-hours.

In the very unfavourable case of trial IV (p. 58) the dose was 100 g per cub. m and the fumigation time 6 hours. This makes 600 gram-hours.

In experiment I in the gassing chamber the dose applied was 70 g per cub. m and the fumigation period 24 hours. This is equal to 1680 gram-hours. In this case all the insects were dead immediately after fumigation. This dose was therefore much higher than necessary.

The other experiments, which were carried out during the week-end, lasted longer than was really necessary, so it is not possible to judge by their results.

The bags of wheat in the gassing boxes in the laboratory were fumigated for six hours with doses of 54 g and 100 g per cub. m, corresponding to 324 and 600 gram-hours. These practical experiments show that the order of magnitude of the gram-hours of M required *in actual practice* must be below 1000.

How is this possible? Probably because ethene oxide dissolves readily in water and M does not. As a result of this, considerable losses may occur which must be compensated by increasing the dose.

In his publication Peters (34) gives a practical dose of 60 to 70 g per cub. m for M. He does not mention in what manner these figures were obtained.

According to Peters the gram-hour values of ethene oxide and M determined in the laboratory are 60 and 275, respectively. For *actual practice* he gives 1200, and 1440—1680 (50 g per cub. m and 60—70 g per cub. m for 24 hours).

His laboratory value for carbon disulphide is 195 gram-hours and for actual practice he advises a dose of 200—500 g per cub. m or 4800—12000 gram-hours. According to the investigations carried out in his laboratory the proportion of ethene oxide to methallyl chloride to carbon disulphide is 60 : 275 : 195. In actual practice this proportion is 1200 : 1440 : 4800 or 60 : 72 : 240.

The above — with the aid of data supplied by Peters himself — proves that the gram-hour value determined in the laboratory under ideal conditions cannot be regarded as a measure for the practical value of a gaseous insecticide. These kinds of determination are at the most of theoretical importance.

Since it is necessary to have some preliminary information about the relative value of a new insecticide before testing it in actual practice, one must have a laboratory method at one's disposal. As such may be considered the experiments with gassing boxes as discussed in Chapter II. These experiments were carried out under "reduced" practical conditions, as a result of which a much better idea of the practical value of the gas is obtained than in experiments in apparatus which may give very accurate results, but which do not provide a true picture of what really happens in actual practice.

*Haber's law. Calculation of practice dose.*

We now come to the question as to whether Haber's law may be applied to M. In the experiments with the accurate laboratory apparatus (page 72 ff) the differences in the results obtained with fumigation periods of 1—4 hours are only very small. For this range of time Haber's law therefore applies. It was not ascertained whether this also applies to a wider range, but this is of very little practical importance.

In the experiments with glass jars filled with wheat (p. 38) it was found that the law did not apply. The figures obtained here, however, were gram-hour values. Now Haber's law does not apply to gram-hour values. So the above statement might be expected. The conclusion that may be drawn from this is that the gram-hour values increase with increasing fumigation times.

Considerable deviations were also noticed in the experiments the aid of gassing boxes described in the beginning of this chapter. In both cases the gram-hour values for fumigation periods of 24 hours and 6 hours bear a proportion to each other of roughly 2 : 1.

It may therefore be expected that also in actual practice the gram-hour value will increase as the fumigation period is longer.

For 3, 6 and 24 hours the values are sufficiently known from the experiments. It would be very convenient, however, if they were also known for the intermediate periods. These may be deduced from the values already known. The figures obtained in the experiments with gassing boxes were chosen for this purpose (page 70). These are admittedly only very rough figures, but for practical purposes they are sufficiently accurate. The proportion for 24 hours, 6 hours and 3 hours was 2.15 : 1.17 : 1. If, in view of the practical experiments carried out, we take a gram-hour value of 480 for six hours, the three values are 881, 480 and 410. If these figures are plotted in a graph a straight line may be drawn through these points. The other gram-hour values may then be read off (graph page 96), for instance, for a fumigation period of 12 hours the gram-hour value is 610. The required dose is then 51 g per cub. m.

The figures apply to "average" cases, for instance for fumigation of not highly absorbent products in properly closed spaces. In unfavourable cases they will be higher, in favourable cases lower. For such cases lines have been drawn in the graph, starting from 50 g per cub. m and 100 g per cub. m applied for six hours. All gram-hour values which may be considered for fumigation with M may be found between these two lines. With the aid of the series of tins (page 41) it may be found out very easily whether a product should be classed among the favourable or the less favourable cases. As far as the fumigation spaces are concerned, vacuum installations and gas boxes should be classed among the favourable cases, old ware-houses among the unfavourable. The lowest dose will be required for fumigation of pulse in a vacuum installation, a much higher one for furs in an old ware-house.

## III. EXPLOSION LIMITS

Methallyl chloride is an inflammable liquid. Its vapour is explosive if mixed with air in certain proportions.

Its explosion range was determined in a tubular vessel (tube test) and was found to be from 105 g per cub. m to 339 g per cub. m.

When determined in a globular vessel (globe test) this range was found to be from 93 g per cub. m to 375 g per cub. m.

So in the most unfavourable case the gas is explosive if the concentration of 93 g per cub. m is exceeded. Below that concentration it is quite safe.

This concentration however, is never obtained in actual practice. Here again a distinction should be made between *dose* and *concentration*. Insects are killed by a *concentration* of 25 g, for instance, during six hours ($c \times t = 150$). In order to obtain such a *concentration*, however, a much higher *dose* should be applied. If a dose of 100 g per cub. m is applied in an old warehouse this does not mean that the work is being carried out within the explosion range, since the *concentration* is much lower than 100 g per cub. m.

It is possible, however, that owing to the gas settling down because of its weight a higher concentration is produced in some places.

For that reason care should be taken that the gas does not come into contact with fire; this applies to other fumigants.

Methallyl chloride may be made non-inflammable by adding carbon tetrachloride to it. Experiments are being carried out to find better materials for this purpose.

## IV. INFLUENCE OF THE TEMPERATURE

The influence of the temperature on the effect of the fumigation was not studied separately. The temperature in practice experiment No. II was 14—15° C. The effect of the gas at that temperature was very good. Insects are not likely to occur in a harmful degree at temperatures under 14° C, so that in my opinion it was of very little use to carry out experiments at lower temperatures.

## V. RELATION BETWEEN THE KIND OF INSECT TO BE CONTROLLED AND THE DOSE

Some kinds of insects are easier to kill with M than others. To obtain some idea about the extent of these differences I made experiments with several species of insects in gassing boxes of 80 litres. These insects all originated from well kept laboratory cultures, though they were not all of the same age. Fumigation time 24 hours, temperature 20° C.

I will only state the minimum dose which, after one week gives 100 % kill.

| Insect | Dose grams per cub. m |
|---|---|
| Araecerus fasciculatus De G. Adult . . . . | 11.6 |
| Galleria mellonella L. Larvae . . . . . . . | 11.6 |
| Calandra oryzae L. All stages . . . . . . . | 12.5 |
| Oryzaephilus surinamensis L. Adult . . . . | 14.5 |
| Dermestes lardarius L. Larvae . . . . . . . | 14.5 |
| Gnathocerus cornutus F. All stages . . . . | 14.5 |
| Tribolium sp. Adult . . . . . . . . . . . | 16.9 |
| Hofmannophila pseudospretella Stt. All stages | 18.0 |
| Ephestia kuehniella Zell. All stages . . . . | 18.5 |
| Calandra granaria L. All stages . . . . . . | 18.75 |
| Cimex lectularius L. All stages . . . . . . | 20.0 |
| Lasioderma serricorne F. Adult . . . . . . | 20.2 |
| Sitodrepa panicea L. All stages . . . . . . | 21.0 } perhaps no |
| Tribolium sp. All stages . . . . . . . . . | 21.0 } minimum |
| Trogoderma sp. Adult . . . . . . . . . . | 26.0 } value |
| Trogoderma sp. Larvae . . . . . . . . . . | 26.0 |

The list shows that the doses required vary from 11.6 to 21 g per cub. m, except for Trogoderma species, which, apparently, are an extreme case.

If one were to take all these differences into account, it would involve a procedure too intricate for actual practice. For my experiments I, therefore, chose one object, viz. Calandra granaria L. which, as is shown in the above list, is one of the highly resistant species, needing 18.75 g per cub. m. Applying the dose calculated for Calandra granaria, all the less resistant species will be killed as well. As for the more resistant species, they show but a slight deviation from Calandra granaria. Since in practice a considerably higher dose must always be applied to compensate for loss of concentration by sorption and leakage, the slight differences in sensibility are, at the same time, made up for.

Only if Trogoderma is concerned it might be necessary to apply a higher dose, whereas in cases such as Araecerus a somewhat lower dose would be sufficient.

## VI. TOXICITY TO MAMMALS

As a last point of investigation I will report here some observations about the toxicity of methallyl chloride to mammals, in comparison to the toxicity of ethene oxide and carbon disulphide.

A gas which is poisonous to insects is also poisonous to higher animals and it will never be possible to find a gas which will kill insects, but which may be inhaled by higher animals or human beings without harm. In this connection I may refer to Peters (35) who remarks: „We shall never see but can only dream of the man who can gas his dwelling for moth and bed bugs, but, at the same time, remain in the rooms that are being fumigated."

It would be foolish to reject these means of control for that reason. A great number of poisons are used by man for all purposes and to the great benefit of society. Poisonous gases used for the control of insects also belong to this category and if the necessary precautions are taken, there is no danger whatever in the application of these products.

In this respect I quite agree with what C. L. Metcalf says in his paper: "Bugaboo or Backbone" (37).

We entomologists may not and cannot tolerate that our best weapons for the fight against insects are knocked out of our hands on loose grounds. It should be considered that insect control is of vast importance. It has not yet been properly realized that a gigantic battle is being waged between two large groups of the animal world: man versus insect, and it is not at all certain that man will conquer in the long run. Metcalf rightly remarks that it is mainly the fear for the unknown that makes people hesitate to use poisonous gases. There is a pipe-system in every house for coal-gas, which is one of the most poisonous gases . . . . !

Our aim should be to find insecticides which are *less* poisonous to human beings than HCN and ethene oxide, for instance, and yet possess good insecticidal activity.

What is the position of methallyl chloride in this respect? I carried out experiments with this product on white rats in comparison with ethene oxide and carbon disulphide. The animals used originated from two breeders. One batch was from a carefully selected breed, while the other batch was derived from a commercial source. No difference was noticed between the experiments upon these two batches.

In the laboratory they were kept at a constant temperature of 22° C. They were fed on $1/3$ of wheat meal and $2/3$ of whole-milk powder. The cages were provided with running water. The weight and the behaviour of the animals was checked regularly. Abnormal specimens were removed.

For fumigating these animals I devised the following apparatus. *A* is a glass aquarium tank with a capacity of about 24 litres, with a loose, three-ply wood cover. The bottom of this cover is provided with soft rubber. It is clamped on to the aquarium by means of 10 rubber bands. A glass cylinder B is fixed in the cover and is big enough to hold a rat of about 200 grams. This cylinder is closed at the top and bottom by means of rubber stoppers. The stopper at the top has two holes to take the thermometer *t* and the glass tube *a*. Underneath the aquarium tank there are two bottles C and D with a capacity of about 10 litres each. The two bottles are connected by means of a glass tube, while a glass tube *f* runs from C to the bottom of the tank. The bottle D is connected to the tube-pump E, the other side of which is connected to the aquarium and the cylinder via the wash bottle F.

At the beginning of the experiment C and D are evacuated. Then the liquid to be evaporated is pipetted into the wash bottle, which is placed in a hot water bath. Air is admitted through *b*, while *c* is closed. The evaporated liquid is carried into the bottles C and D by the air, which process may be checked by means of the manometer G. All the liquid should be evaporated before the atmospheric pressure in the two bottles has been restored. As soon as this the case *b* is closed and *c* and *d* are opened, while *a* remains closed.

Now the pump is started. The gas circulates through A, C and D until a homogeneous mixture is obtained. Then B is opened at the top and a rat is placed inside the cylinder. It is closed again and the bottom stopper is pushed out by means of the thermometer. The rat then drops into the tank. The cylinder is therefore used as a sluice. The animals remained in the apparatus, which had a total capacity of 46 litres, for 25 minutes at the most. The rubber strips could be removed very quickly, so that the animals could be easily taken out at the end of the experiment. (Fig. 3, photograph 6).

In this apparatus rats were gassed with M, ethene oxide and carbon disulphide. In all cases the dose was 100 g per cub. m, the temperature was 20—21° C.

The *behaviour* of the rats which were gassed was as follows:

*Methallyl chloride.*

They ran around restlessly sniffing and blinking. It was evident that they found it difficult to breathe. The movements

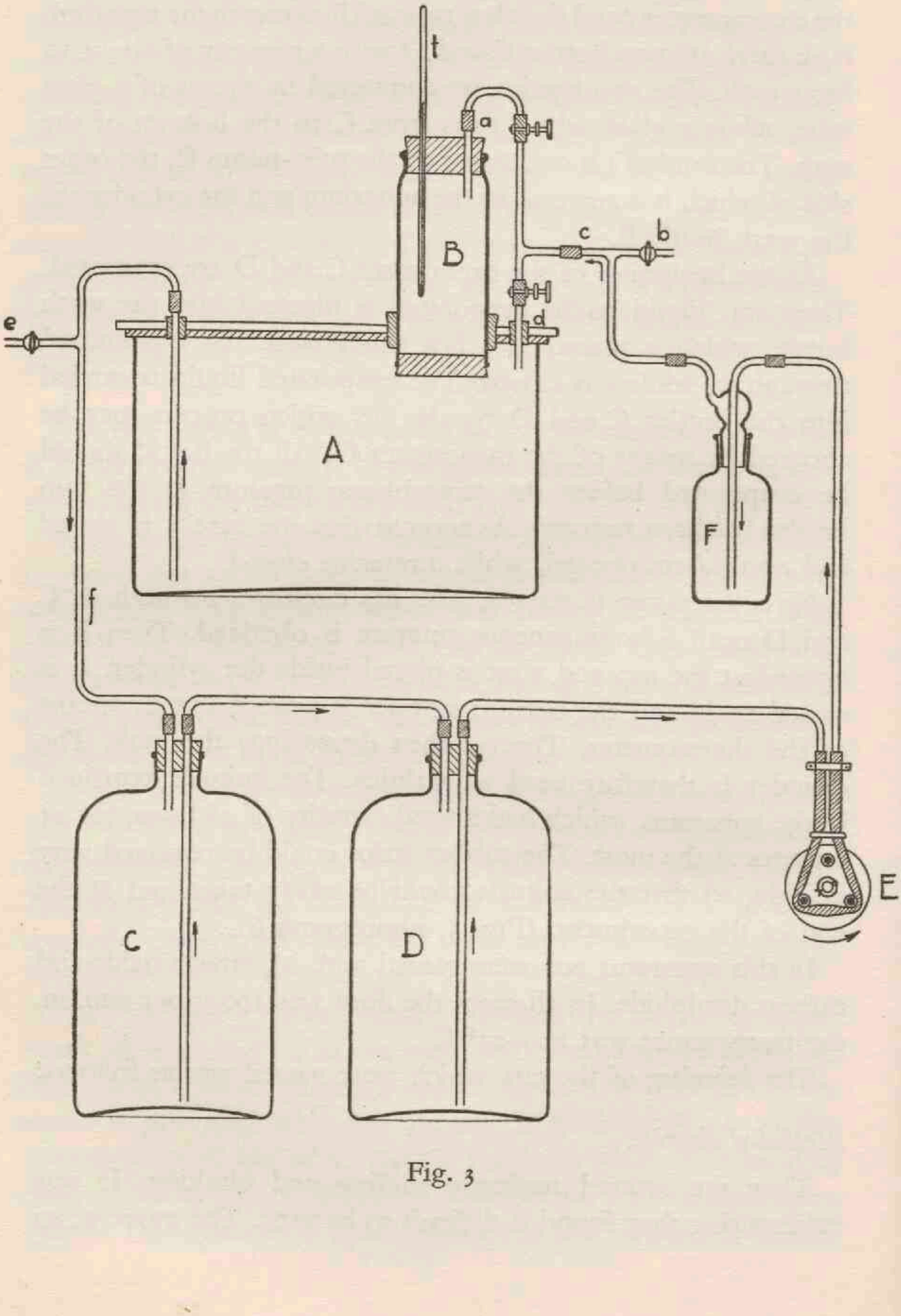



Fig. 3

became less and less decisive and after a few minutes they became unconscious and were lying on their sides. Generally foam appeared at the nose. After fumigation they came to within a few minutes. Legs and ears were bright red, later they acquired a bluish colour.

Dissection of the succumbed ones showed that the lungs had been affected (filled with liquid, lung oedema).

*Ehene oxide.*

The animals appear to remain normal. There is nothing peculiar to be seen. Dissection showed that the lungs and sometimes also the liver had been affected.

*Carbon disulphide.*

They run around, are restless and their movements are spasmodic. In many cases they become very wild and afterwards unconscious. After they have been taken from the tank they sometimes die with a shock. In other cases they were temporarily or permanently paralysed.

Dissection did not provide any further particulars.

All the animals were weighed once a week before and after fumigation.

Immediately after fumigation it was found that their weight had decreased a little. It is remarkable that in many cases a marked increase of weight occurred a short time after fumigation, which was especially the case with M.

The results of the fumigation are given in the table on page 90. The sign + denotes that the animals succumbed as a result of the fumigation. Generally death occurred one or a few days after fumigation.

From these results it is clear that there is a very great difference between the effects of ethene oxide and M and that the latter is only a little more poisonous to higher animals than is carbon disulphide.

| Fumigation period | Ethene oxide | Methallyl chloride | Carbon disulphide |
|---|---|---|---|
| 1½ minutes | 13 — | — | — |
| 2 ,, | 26 — 2 + | — | — |
| 3 ,, | 14 — 26 + | — | — |
| 15 minutes | | 51 — | 6 — |
| 17½ ,, | | 16 — 5 + | 8 — |
| 20 ,, | | 24 — 15 + | 17 — 2 + |
| 25 ,, | | 2 — 4 + | 9 — 9 + |

With ethene oxide the animals can stand at the most a fumigation period of 1½ minutes, while this period is 15 minutes in the case of M and 17½ minutes in the case of carbon disulphide. In all cases the dose was 100 g per cub. m.

This shows a great advantage of M as compared with ethene oxide.

Furthermore the irritating odour of M and the irritating effect upon the eyes are a clear warning that this gas is present. It is out of the question that any one would by accident enter a room which is being fumigated and remain there. Even people who lack the sense of smell would be warned by the irritation of the eyes. Even at very low concentrations its presence may be easily detected. Ethene oxide does not possess this property.

Yet it remains essential for persons who enter the rooms which are being fumigated to wear a gas mask. When the liquid is being atomized, this mask should also be provided with a *mist* filter.

## VII. CONCLUSIONS FROM THIS SUPPLEMENTARY INVESTIGATION

1. The approximated c × t value of M for a fumigation period of 1, 2, 3, or 4 hours is about 160, in any case lower than 200.

2. The c.t figure cannot be regarded as a measure for the practical value of a gaseous insecticide.
3. In actual practice the gram-hour value of M lies between 500 and 1000, dependent on the conditions under which it is applied. If losses are high it may also be higher than 1000.
4. M is considerably less poisonous to higher animals than ethene oxide and only a little more poisonous than carbon disulphide.

# GENERAL SUMMARY

Experiments were carried out with methallyl chloride as a gaseous insecticide.

It was shown that the activity of this product is very high. Furthermore it has an irritating effect on the insects, so that it is not necessary to add other irritants.

If the gas is properly applied the quality of most products is not affected. A method was worked out for the objective determination of the effect on the taste of the products. The germinating power of seeds is not affected; bulbs, tubers, and many plants are not damaged.

The *concentration* to be applied — not to be confused with *dose* — lies far below the explosion limit.

It is only a little more poisonous to higher animals than carbon disulphide and considerably less so than ethene oxide. Several practice trials are described.

It was shown that the so-called c.t value determined in the laboratory is of no value for comparing the effect of gaseous insecticides.

A graph is drawn by which to find the dose required in practice for different fumigation periods and under different conditions.

# INSTRUCTIONS
# FOR THE USE OF METHALLYL CHLORIDE IN ACTUAL PRACTICE

These instructions give the approximate doses of M required in different cases.

The effect is expressed in gram-hours, that is, the number of grams required multiplied by the number of hours. This number of hours is the period of time that passes between the atomizing of the gas and the moment at which ventilation is started.

The possible cases have been divided into three categories in which a small, an average or a large dose is required, both with respect to the products and the spaces. Products which absorb a large quantity of the gas require a high dose. A large dose is also required in rooms containing a lot of absorbent material, such as old wood, carpets, curtains, or if leakage occurs.

*Products.*

*Small dose* — all pulse, coffee beans.

*Average dose* — all kinds of grain, all kinds of dried fruit, cocoa beans.

*Large dose* — almonds, nuts, beeswax, furs, carpets, furniture. Probably also tobacco and cattle-cakes.

*Spaces:*

*Small dose* — vacuum installations and special gassing chambers.

*Average dose* — properly sealed warehouses of reinforced concrete.

*Large dose* — ordinary warehouses and factories. Dwellings.

The smallest dose is therefore required for pulse in vacuum installations, for instance; the largest dose for furs in old warehouses with a lot of mouldered wood.

## FOR WHAT TIME MUST FUMIGATION BE APPLIED?

Some products, such as pulse and cocoa beans can stand a long fumigation period very well. Other products such as grain should not be fumigated for more than 12 hours and if possible even for a shorter period of time.

Generally the duration of the fumigation should be shorter as the number of gram-hours required is higher. It is advisable, however, to use a dose not higher than 80 g per cub. m. The parts of the lines in the graph which correspond to a higher dose are dotted.

Empty rooms and houses may be fumigated for a long time if this is desired. Up to now the gas has never been found to affect metals, furniture or colours. Care should be taken that objects which are likely to be damaged do not come into direct contact with the mist blown off from the nozzle.

*The number of gram-hours required for the fumigation times chosen here, are indicated for each of the three categories in the graph page* 96.

## INFLUENCE OF THE QUANTITY OF THE GOODS ON THE DOSE

The extent to which the space is filled may also influence the dose required. In general it may be said that with products which absorb only a small quantity of gas and therefore only need a small dose, this dose should be even a little lower if the space contains a larger quantity of the product. In the case of products which require an average dose, this dose remains the same even if the rooms contain a larger quantity of the product. For products which already require a large dose, because they absorb a large quantity of the gas, the dose should be increased if the space contains a large quantity of these products.

## VENTILATION

After fumigation the rooms should be well ventilated for from 6—24 hours, the period being dependent on the conditions.

## FIRE AND LIGHT

All open fires and lights should be extinguished, also pilot flames of gas heaters.

## MISCELLANEOUS

During fumigation the temperature should be at least 15° C, preferably a little higher.

Any person entering the rooms which are being fumigated must wear a gas mask provided with a carbon filter, e.g. Degea Canister A. During the time the liquid is being atomized, the mask should be provided with a mist filter.

If necessary the rooms should be sealed before fumigation for which purpose strips of wood, putty, strips of paper, etc. may be used.

## EXAMPLES OF HOW TO DETERMINE THE DOSE

Suppose pulse must be fumigated in a gassing chamber. A small dose is required. The duration of the fumigation is fixed at 24 hours. According to the graph the number of gram-hours is 560. The dose per cub. m should then be 560 : 24 or, roughly, 23 g.

If the same products are to be fumigated for 10 hours, the number of gram-hours required is 370 and the dose is 37 g per cub. m.

Suppose bags of wheat must be gassed in a ware-house constructed of reinforced concrete which can be properly sealed. This is an average case. The best fumigation time for wheat is less than 12 hours. The fumigation period may be fixed at 8 hours. The number of gram-hours required is 520 read from the graph. The dose should be 520 : 8 or 65 g per cub. m.

## ADDENDUM

### *Method for obtaining test insects*

I will describe here the method which I succesfully applied for obtaining Calandra species. With slight alterations this method may be applied for many other insects.

The material needed for a laboratory culture must be obtained from storages, in the case of Calandra, for instance, from granaries, if possible from more than one. If this is not done it may occur that a selected strain is obtained.

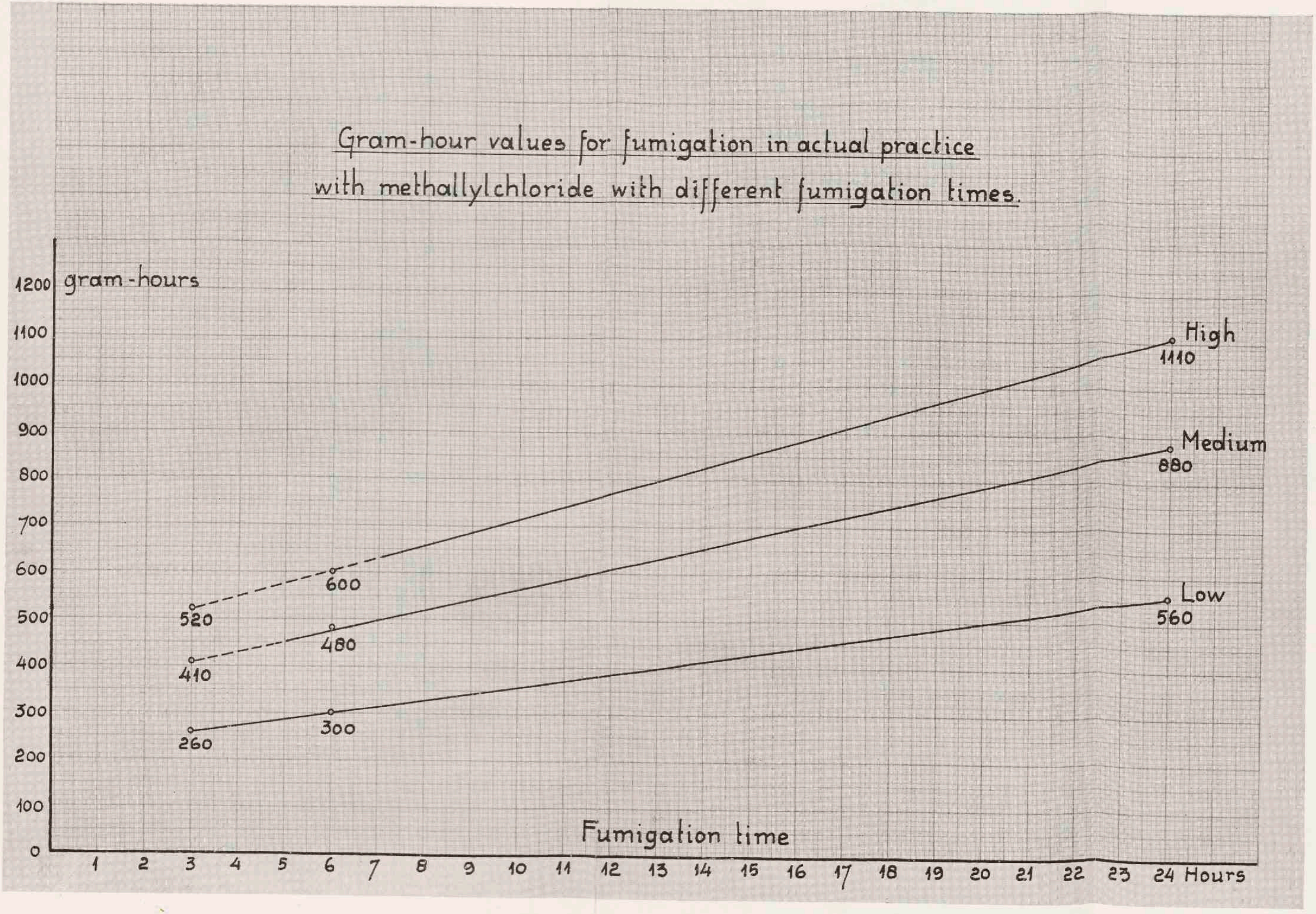
The collected Calandra are transmitted on to wheat of good quality and placed in an incubator at a constant temperature between 20—28 C.

The cultures may not be overcrowded. Overcrowding is indicated by migration of the insects out of the wheat. To detect this the cultures must be observed while they are standing in a quiet place, because a tendency to migrate also occurs if the insects are disturbed.

One month after starting the culture the adults are screened of and destroyed. About one or two weeks later their progeny emerge from the wheat. A sufficient number of these are collected and a fresh culture is started with them. The natural rate of mortality of these adults is also determined. If this exceeds a few percents in one week, other material must be looked for. Otherwise, the insects are kept for one month again in the wheat; at the end of this period they are screened off and destroyed.

The descendants that hatch after some weeks are now screened off daily. The age of these adults is thus known exactly.

One month after hatching, the Calandra may be used for


Gram-hour values for fumigation in actual practice
with methallylchloride with different fumigation times.
gram-hours
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
High
1110
Medium
880
Low
560
520
600
410
480
260
300
Fumigation time
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 Hours

trials. The superfluous adults are used to start new cultures.

It is advisable to keep the cultures in an incubator at 27—28° C, while the adults that have been screened off are placed in an incubator at 20° C, which is the same temperature as that at which the experiments are carried out.

The most suitable relative humidity is about 80 %.

As containers for the cultures I used aquarium tanks with a piece of flannel and a glass pane. The adults that had been screened off were put into jars as described on p. 34; a piece of cupper gauze was soldered into the cover of the jar.

*List of insects which were used for experiments with methallyl chloride*

Besides upon Calandra species, the effect of M was tested upon many other insects. A list of the insects which, as was ascertained in our experiments, may be controlled with methallyl chloride, is given below. The varieties marked with * were used in practice trials. The common names of the insects were obtained from a list published by the American Association of Economic Entomologists (38). The names between brackets did not occur on this list.

Tenebrioides mauretanicus L. Cadelle.
Oryzaephilus surinamensis L. Saw-toothed grain beetle.
* Dermestes lardarius L. Larder beetle.
Attagenus piceus Ol. Black carpet beetle.
Lasioderma serricorne F. Cigarette beetle.
* Sitodrepa panicea L. (Drug store beetle.)
Ptinus tectus Boield. (Spider beetle.)
Tenebrio molitor L. Yellow meal worm.
Gnathocerus cornutus F. (Broad horned flour beetle.)
* Tribolium sp. Flour beetles.
Araecerus fasciculatus De G. Coffeebean weevil.
Bruchus rufimanus Boh. Broadbean weevil.
* Endrosis lacteella Schiff.
Plodia interpunctella Hb. Dried fruit moth.
* Ephestia elutella Hbn. (Cacao moth.) Tobacco moth.

* Ephestia kuehniella Zell. Mediterranean flour moth.
* Paralispa (Aphomia) gularis Zell. (Nut moth.)
* Hofmannophila (Borkhausenia) pseudospretella Stt. (Seed moth.)
Galleria mellonella L. Wax moth.
Achroea grisella F. (Small wax moth.)
* Phthorimaea operculella Zell. (Potato moth.)
Cimex lectularius L. (Bed bug.)

*List of products which were fumigated with methallyl chloride*

The following products were successfully fumigated both in the laboratory and in actual practice (* only in the laboratory).

Wheat, maize, rice, peas, cocoa beans, tobacco*, apricot-stones, almonds, hazel-nuts, dried apricots, various kinds of raisins and currants, sugar, corn-flour, tapioca*, vermicelli*, grated cocoa-nut, corn-flakes, ginger, pressed copra-cakes*, furs, beeswax*, carpets and furniture.

The following goods were adversely affected by the gas: *Flour* became musty. There is no objection whatever to fumigation of flour-mills, as long as the stock of flour itself is not fumigated.

*Potatoes* also became musty.

*Shelled walnuts acquired* a somewhat darker colour.

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# STELLINGEN

1. Het experimenteel in het laboratorium bepaalde Habergetal heeft voor de onderlinge vergelijking van gasinsecticiden geen waarde.

   Dit proefschrift blz. 76 f.f.

2. Bij de bestrijding van insecten met chemische middelen bestaat het gevaar, dat door overleven van de sterkste individuen een averechtsch effect wordt bereikt.

   Dit proefschrift blz. 15.

3. Chemische middelen kunnen bij de bestrijding van schadelijke insecten niet worden gemist.

4. Bij het onderzoek van den invloed van chemische middelen op zaaizaden dient behalve de kiemkracht ook de verdere ontwikkeling te worden nagegaan.

   Dit proefschrift blz. 48.

5. De meening van FLURY, dat de oorlog met gassen „humaner" is, dan de oorlog met explosieve stoffen, is onjuist.

   FLURY UND ZERNIK. *Schädliche Gase*, 1931

6. Bij de bemesting van land- en tuinbouwgewassen wordt te weinig aandacht besteed aan de mogelijkheid tot natuurlijke ontwikkeling van koolzuur.

7. Kunstmatige koolzuurbemesting van gewassen op het vrije veld is uitvoerbaar en heeft groote praktische waarde.

8. Er dienen proeftuinen aangelegd te worden, waarin de genotypen van land- en tuinbouwgewassen, die bij de selectie terzijde gesteld worden, bewaard blijven.

9. Het beinvloeden van de kiemcellen van land- en tuinbouwgewassen door Röntgenbestraling e.d., met het doel kunstmatig een groot aantal nieuwe varieteiten te doen ontstaan, is economisch niet te verdedigen.

10. Het geelziek der hyacinthen kan bestreden worden door verandering van cultuurmethode.

11. De mededeeling van KABOS, dat de narcisvlieg *Merodon equestris* Fabr. door een warmwaterbehandeling bij 43.5° C. lang niet altijd gedood wordt, is onjuist.

*Entomologische Berichten* Mei 1939

12. Voor bestrijding van de narcisvlieg is het noodzakelijk, dat verwilderde narcissen in bosschen, parken en tuinen, gelegen in de bloembollenstreek, vernietigd worden.

13. De fabricage van suiker uit beetwortelen kan vereenvoudigd worden, door de uit de wortelen verkregen snijdsels te drogen en op te slaan en de rest van de bewerking over het geheele jaar te verdeelen.

14. Het construeeren van curven uit de resultaten van biologische proefnemingen blijve beperkt tot het allernoodzakelijkste.

15. Geregelde kunstmatige zuivering van de lucht in laboratoria, fabrieken en werkplaatsen zal de arbeidsprestaties belangrijk verhoogen en het aantal ziektedagen verminderen; zij dient van overheidswege te worden voorgeschreven.

16. Bij het onderwijs aan de Nederlandsche Universiteiten wordt onvoldoende aandacht besteed aan de toegepaste biologie.

17. Het instituut der Volkstuinen verdient ondersteuning van overheidswege.

18. Gelijkstelling van allen is gelijkstelling van ongelijkheden.