THE INFLUENCE OF COMMODITY, PACKING MATERIAL AND THE PROPERTIES OF THE FUMIGATION CHAMBER ON THE CONCENTRATION OF HYDROCYANIC ACID IN THE GAS PHASE [1]

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SUMMARY

The results of a number of fumigation experiments with HCN are discussed. The concentration of the fumigant in the gas phase is greatly dependent on the nature and quantity of the product fumigated and on a number of properties of the fumigation chamber.

Consequently it is proposed to bring about a general improvement in the standard of chambers in which quarantine fumigations are carried out. The use of the concentration-time products for the various pests to be fumigated is also recommended.

In view of the increasing trade in vegetable products the measures taken to prevent the spread of noxious insects from one country to another grow increasingly important. As fumigation forms part of these precautions, which are international in character, it is advisable to standardize on gas treatments as much as possible.

To achieve such a standardization it is necessary to know the influence of various factors on the result of fumigation. It was not the intention to determine the influence of these factors in a purely scientific way. Our experiments concern mainly applied research and observations in practice, which confirm the results of English and American research for the greater part. They also prove how important it is to take account of these factors in practice.

Considering it is only the fumigant in the gas phase (free gas) that has an effect on insects and mites, the question arises as to how far the concentration of this free gas is influenced by properties of the commodity and packing material. The properties of the chamber in which the fumigation is carried out have also to be taken in consideration. Consequently it is necessary to determine whether certain factors (viz. sorption by the commodity, the packing material or by the walls) can have such an influence that ultimately the control is inadequate although the prescribed dose has been applied.

We have confined our work to the use of hydrocyanic acid. Earlier research (SINCLAIR and LINDGREN, 1952) has shown that hydrocyanic acid is more strongly sorbed by the commodity and by the walls of the fumigation chamber than are other gases. In spite of this unfavourable property the use of hydrocyanic acid is preferred in a number of West European countries. One reason for preference is that the toxicity of hydrocyanic acid to insects is less dependent on the temperature than is the toxicity of other gases. This fact is especially important for the control of the San José scale, an operation which is mainly carried out during the winter season at temperatures just above freezing point.

Moreover it is easier to carry out fumigations in bulb storehouses with

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hydrocyanic acid than with other gases. These factors have led to the rather frequent use of hydrocyanic acid fumigation in the Netherlands.

I The influence of commodity and packing material

a Sorption

In many cases plant material is fumigated while it is packed in crates, straw, reed or in earth or peat dust. Two series of experiments were carried out in order to investigate the influence of these packing materials on the concentration of the fumigant in the gas phase.

1 dose: 2 and 4 grams of Calcid (equivalent to about 1 and 2 grams of HCN) per cubic metre respectively.
The concentration of free gas was determined:
in an empty chamber
in a chamber containing 70 kilograms of bulbs and 80 kilograms of deal crates respectively.

2 dose: 6 grams of HCN per cubic metre.
The concentration of free gas was determined:
in an empty chamber
in a chamber containing 80 kilograms of ligneous material, 80 kilograms of dry crates, 80 kilograms of straw, 80 kilograms of dry sand, 80 kilograms of earth and 80 kilograms of damp peat dust respectively. The influence of concrete plates was also examined.

All fumigations were carried out in an experimental fumigation chamber (see fig. 1 and 2) belonging to the Plant Protection Service at Wageningen. Capacity 3 cubic metre, iron walls covered with grey oil paint. Air circulation 120 cubic metre per hour. Temperature during the fumigations 17–19° C. The relative humidity varied from 65–70 %.

With a few exceptions all experiments were carried out in duplicate. The HCN determinations were all carried out in duplicate.

The HCN determinations were carried out by leading the gas mixture from the fumigation chamber through a solution of iodine 0.02 n (0.5 ml or 5 ml) to which $NaHCO_3$ and a few drops of a starch solution were added. The

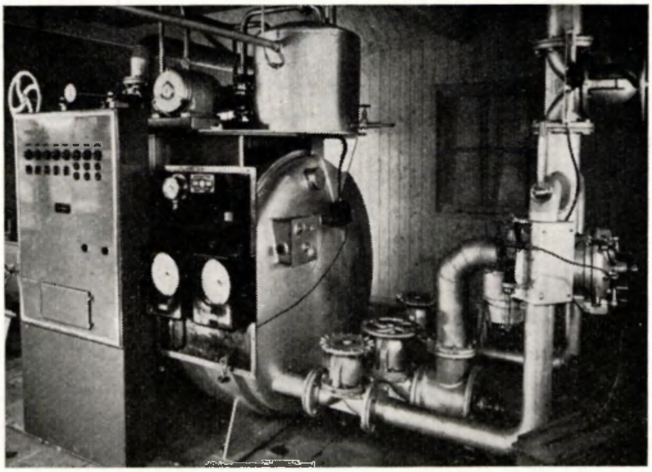

FIG. 1 SIDE VIEW OF EXPERIMENTAL FUMIGATION CHAMBER. Left: dashboard. Top: vacuum pump. Right: circulation and dosing system.

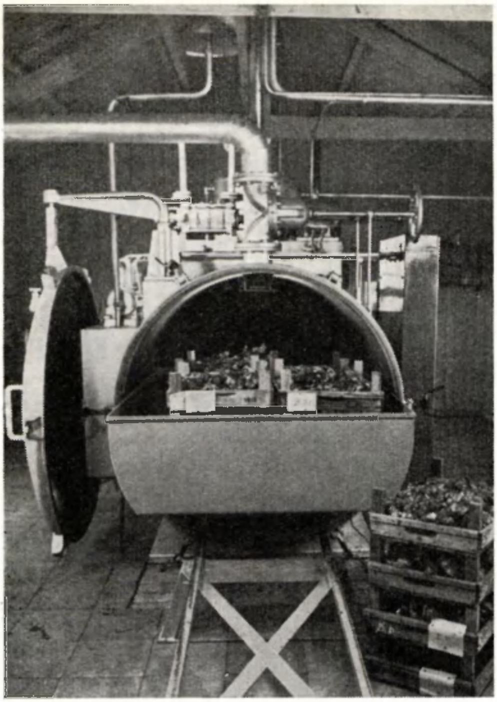

FIG. 2 FRONT VIEW OF EXPERIMENTAL FUMIGATION CHAMBER WITH SMALL WAGON, CONTAINING CRATES OF BULBS. Left : heating elements with water pump ; right : dashboard.

volume of gas mixture required to decolorize the solution was measured. In order to calculate the HCN concentration it was assumed that the quantity of free iodine in 10 ml solution of 0.001 n was equivalent to 0.135 mg of HCN.

Between two succeeding fumigations there was a considerable lapse of time during which the chamber was ventilated to prevent sorbed gas affecting a following experiment.

The fumigations with 2 and 4 grams of Calcid were carried out in accordance with practical treatments of storehouses where bulbs are fumigated for the control of aphids and mites. The fumigations with 6 grams of HCN were similar to the statutory gas treatment of woody plants imported into the Netherlands.

1 The levels of the concentration of free gas when using 2 grams of Calcid per cubic metre ; see fig. 3.

From the observations the following facts may be inferred. HCN is liberated relatively slowly from the Calcid placed in the empty cell. During the first hour the gas concentration increases fairly uniformly, viz. up to about 0.48 grams of HCN per cubic metre. After two hours the concentration reaches 0.52 grams of HCN per cubic metre ; subsequently there is only a slight increase.

The levels of the gas concentration during the fumigation of 70 kilograms of bulbs are indicated by two lines. The experiments were actually carried out with an interval of one month. The two series of results could not be combined as the bulbs had slightly dried up during this period. The bottom line represents the concentration of free gas during an experiment on February 15th ; the top line that during an experiment on March 16th. At

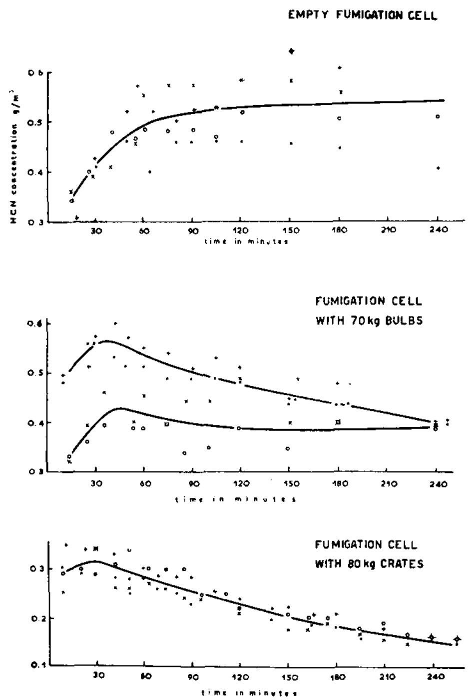

FIG. 3 THE CONCENTRATION OF THE FREE GAS DURING A FUMIGATION WITH 2 g CALCID PER M^3 IN AN EMPTY CELL, AND IN THE SAME CELL WITH BULBS AND WITH CRATES.

first the HCN gas appears to be liberated more quickly than it is sorbed by the bulbs. After 45 minutes, however, the rate of sorption exceeds the rate of liberation of the gas, thus causing a decrease of concentration. The damper bulbs of February 15th appeared to sorb considerably more gas than the drier bulbs of March 16th.

While fumigating crates, the concentration decreases gradually to very low values (0.15 grams of HCN after four hours).

The data produced by the fumigations with 4 grams of Calcid agree with that of the series described above.

2 The levels of the free gas concentration with the use of 6 grams of HCN per cubic metre are shown in figures 4 and 5.

In these fumigations HCN was obtained by the reaction of NaCN and H_2SO_4.

Soon after dosing an equilibrium is set up between free and sorbed gas in the empty chamber, after which the gas concentration runs in a straight line (4.3 grams of HCN per cubic metre).

Ligneous plant material sorbs relatively little HCN.

The following conclusions may be drawn from these observations:

The experiments show, that the concentration of free gas is strongly influenced by the presence of timber, straw, soil and damp peat dust, these materials often being present in the chamber during fumigation of plant material.

Straw in particular, which during winter is used as packing material sorbs much HCN and thus causes a great reduction of the free gas concentration. In view of the figures obtained it may be enquired whether it is possible for the gas concentration to drop in such a way as a consequence of straw

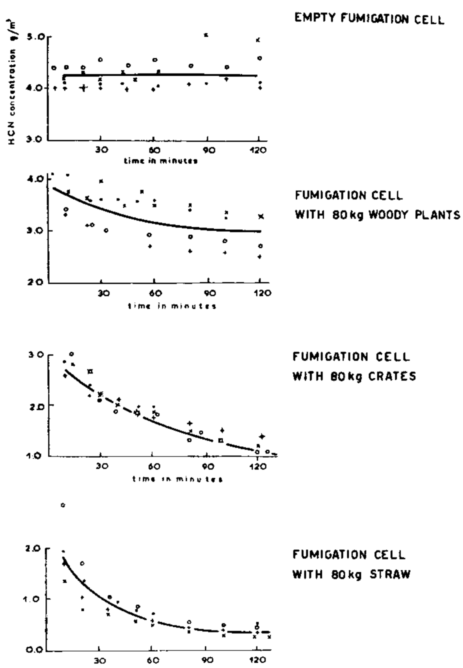

FIG. 4 THE CONCENTRATION OF THE FREE GAS DURING A FUMIGATION WITH 6 g HCN PER M³ IN AN EMPTY CELL AND IN THE SAME CELL WITH WOODY PLANTS, CRATES AND STRAW.

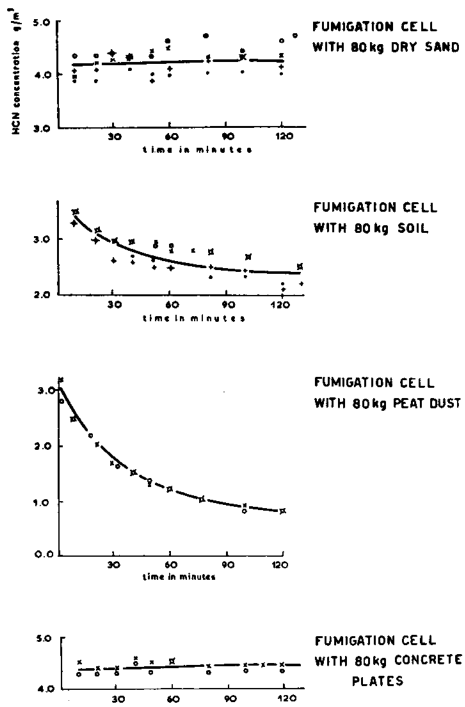

FIG. 5 THE CONCENTRATION OF THE FREE GAS DURING A FUMIGATION WITH 6 g HCN PER M³ IN A CELL WITH DRY SAND, SOIL, PEAT DUST AND CONCRETE PLATES.

packing that there may not be sufficient gas to kill noxious insects on the plants. It is important to pay further attention to this problem in connection with the fumigations of imports with HCN directed against the San José scale.

Crates also sorb a considerable dose of HCN. 80 kilograms of crates with a total area of 21 m² dry timber were experimentally fumigated. This relatively small area causes considerable loss of concentration. This is important with regard to fumigations of bulbs on wooden scaffoldings or in crates and often in wooden storehouses, and can undoubtedly lead to a considerable fall in concentration.

In the above experiments with 2 and 4 grams of Calcid per cubic metre and 6 grams of HCN per cubic metre the timber is found to sorb about 70% of the initial dose of HCN. This high percentage agrees with the figures published by BARR, THOROGOOD and VAN REST (1940). They also found that the large quantities of HCN which timber can sorb are only liberated very slowly after fumigation. Consequently even after a considerable lapse of time it is very dangerous to enter rooms in which there has been sorption by timber.

An equal weight of concrete plates sorb practically no HCN. A later experiment showed that a larger quantity of concrete plates with an area of about 19 m² (using 6 grams of HCN per cubic metre) causes a drop of concentration to about 2.8 grams of HCN after two hours.

As the ultimate concentration with 21 m^2 of crates after two hours is 1.1 gram of HCN, it can be concluded that for area timber sorbs more HCN than concrete plates. Nevertheless the drop in concentration with concrete should not be disregarded.

Peat dust (77.8 % humidity) shows considerable sorption, while soil (9.1 and 7.4 % humidity) shows a moderate sorption. Dry sand sorbs practically no HCN. The presence of damp peat dust as well as soil, which on the whole contains more water than the soil used in the experiment, may also have a great effect on the levels of the concentration.

Shipinov (1940) previously found that under certain conditions soil can sorb considerable quantities of HCN.

b Penetration

In view of the fact, mentioned above, that ligneous plant material which has to be fumigated on importation is often packed in straw or reed, investigations were made to determine how far straw as a packing material prevents penetration of the gas. For this purpose three lots, each containing 1000 young elms, found on import inspection to be infected by San José scale, were treated in the following way:

a tightly packed in straw, fumigated with HCN ;
b not packed, fumigated with HCN;
c not treated.

The fumigations were carried out on February 6th, 1953 in a mobile fumigation chamber with a capacity of 16 m^3. 5 grams of HCN were used per m^3; the fumigation lasted 30 minutes. The circulation during fumigation was 640 m^3 per hour. In this case the fumigations were carried out in a large chamber so as to eliminate as far as possible the influence of gas sorption by the straw.

After fumigation the elms were planted in an isolated experimental plot together with an untreated lot for comparison. In September and October the development of San José scale on this material was investigated. The results are shown in table 1.

Table 1 Numbers of living scales after fumigation in straw packing (a) and not packed (b), in comparison with non-treated (c).

Number of elms examined	Number of living specimens of San José scale			
	full-grown	black scale	white point	larvae
(a) 435	108	30	42	238
(b) ca 500 . . .	no living specimens of San José scale			
(c) ca 500 . . .	numerous specimens of live San José scale			

This experiment shows that a tight straw packing can prevent penetration of HCN gas to such an extent that the kill is insufficient. The conclusion is that straw packing has to be opened to admit the gas.

II The influence of the properties of the fumigation chamber

Fumigations with HCN in bulb storehouses are carried out regularly in order to control aphids and mites. Several experimental fumigations were carried out in order to determine the levels of the gas concentration as effected by varying conditions.

a Differences between storehouses

Results of fumigations in a modern, well-sealed storehouse (capacity of 345 m^3; plastered walls) were compared with those in an older wooden storehouse (capacity 220 m^3) not so well-sealed.

An investigation was also made into the influence of external factors such as strong wind on the levels of the gas concentration in the wooden storehouse which was not so well-sealed.

To avoid complications these fumigations were carried out when the storehouses were empty. During the treatment there was no circulation. Details about these fumigations are given in table 2.

Table 2 Conditions during comparative fumigations in two bulb storehouses.

	Date of fumigation	Quantity of Calcid per m^3	Conditions in storehouses		External factors, wind velocity
			temp. in centigrades	relative humidity	
Storehouse A (well-sealed)	25-3-54	2 grams	17–20° C	66 %	–
Storehouse B (1) (not so well-sealed)	9-3-54	4 grams	15° C	74 %	1½–3½ (E.)
– do – (2)	25-3-54	4 grams	13½–14½° C	74 %	5½–6½ (S.W.)

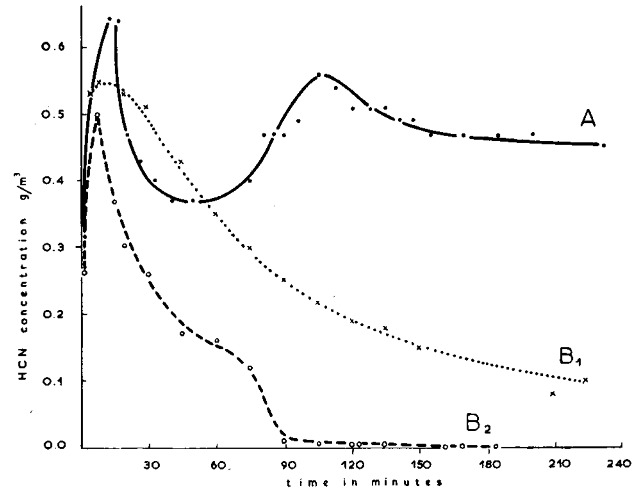

Fig. 6 The concentration of the free gas in a well-sealed bulb storehouse A (initial dose 2 g calcid per M^3) and in a not so well-sealed bulb storehouse B (initial dose 4 g calcid per M^3) for two data. No circulation.

The levels of the gas concentration determined as described on page 116 are shown in fig. 6.

Despite the fact that in storehouse B a double application of Calcid was given in each case to compensate for leakage, the concentration of free gas was ultimately considerably lower.

In storehouse A the concentration levels show two peaks. These were also found some days later in a subsequent test. The second peak presumably arose because at a certain moment during the liberation of the gas the sorption of the walls decreased more rapidly than the liberation of the gas.

The strong wind during the fumigation on March 25th (B2) caused a rapid and sudden decrease in the gas concentration. After 90 minutes practically all HCN has disappeared.

The following conclusions may be drawn from these observations:

If a storehouse does not shut sufficiently tightly, the leakage cannot in all cases be compensated by an overdose.

External factors (wind velocity) have a great effect on the gas concentration in storehouse which do not shut sufficiently tightly. In this case, there was a strong wind, practically no HCN was left in the storehouse 1½ hours after the application.

b Circulation during fumigation of bulb storehouses

In the well-sealed storehouse A the influence of circulation (3500 m^3/h) of the gas mixture on the levels of the free gas concentration was also investigated.

The tests were carried out when the storehouse was empty, when it was filled with crates, and finally when it was filled with crates packed with hyacinths.

The data relating to these fumigations are given in table 3. In all cases fumigation was carried out with 2 grams of Calcid per m^3.

Table 3 Conditions during comparative experimental fumigations in storehouse A.

Date of fumigation	Contents of storehouse	Conditions in the storehouse		
		circulation or no circ.	temp. in centigrades	relative humidity
30-6-55	empty	no circ.	16.7° C	85 %
	empty	circ.	17.8° C	77.5 %
8-6-55	2000 crates	no circ.	15.8° C	69 %
	2000 crates	circ.	15.7° C	69 %
18-8-55	2600 crates + 39000 kg hyac.	no circ.	32° C	61 %
	2600 crates + 39000 kg hyac.	circ.	32° C	58.5 %

The gas concentration was determined as indicated on page 116. The tests were carried out simultaneously at two different altitudes, viz. 0.20 and 2.80 metres above the ground. The levels of the concentrations are shown in figures 7, 8 and 9.

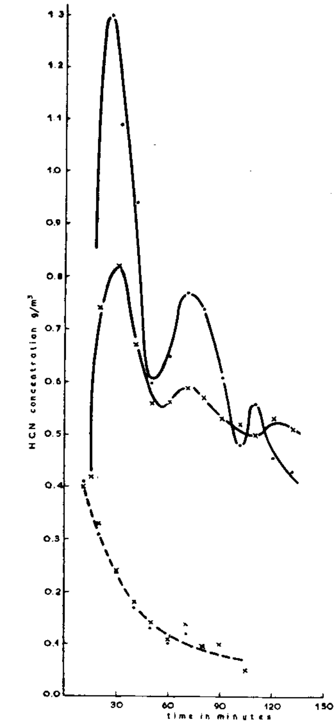

FIG. 7 THE CONCENTRATION OF THE FREE GAS DURING A FUMIGATION WITHOUT (——) AND WITH (- - -) CIRCULATION IN AN EMPTY BULB STOREHOUSE.

. . . . samples taken 0.20 m above the ground
××× „ „ 2.80 m „ „ „
Initial dose 2 g Calcid per m³.

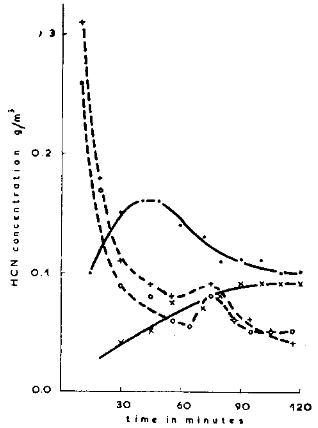

FIG. 8 THE CONCENTRATION OF THE FREE GAS DURING A FUMIGATION WITHOUT (——) AND WITH (- - -) CIRCULATION IN A BULB STOREHOUSE WITH 2,000 CRATES.

. . . . / o o o } samples taken 0.20 m above the ground
××× / +++ } „ „ 2.80 m „ „ „
Initial dose 2 g Calcid per m³.

Each of these figures shows that as a result of circulation the concentration of free gas has quite different levels than when there is no circulation during fumigation. Furthermore they show that the differences between the gas concentration at 0.20 and 2.80 metres are greater without than with circulation of the gas mixture. In two cases the concentration just above the ground (where the Calcid was used) was higher that at 2.80 metres and in one case the reverse was true. This is probably accidental. In one case, of course, the Calcid may have been in a more unfavourable position with regard to the measuring point near the ground.

In the empty storeroom the concentration levels without circulation again

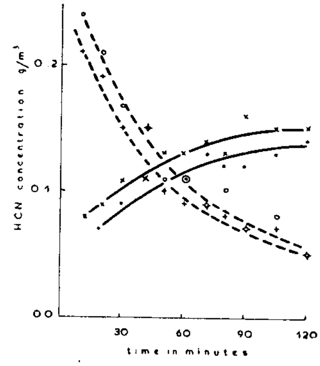

FIG. 9 THE CONCENTRATION OF THE FREE GAS DURING FUMIGATION WITHOUT (——) AND WITH (- - -) CIRCULATION IN A BULB STOREHOUSE WITH 2,600 CRATES PACKED WITH 39,000 kg HYACINTH BULBS.

. . . . } samples taken 0.20 m above the ground
o o o }

××× } „ „ 2.80 m „ „ „
+++ }

Initial dose 2 g Calcid per m³.

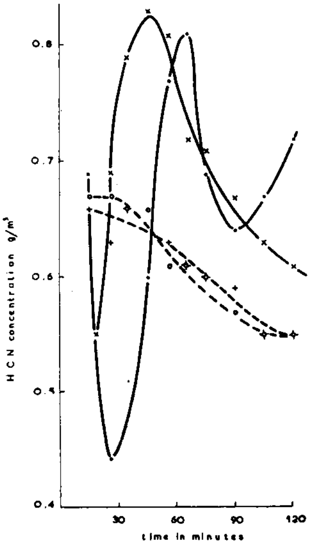

FIG. 10 THE CONCENTRATION OF THE FREE GAS DURING FUMIGATION WITHOUT (——) AND WITH (- - -) CIRCULATION IN A FUMIGATION CHAMBER WITH WALLS COATED WITH OIL PAINT.

. . . . } samples taken 0.20 m above the ground
o o o }

××× } „ „ 2.00 m „ „ „
+++ }

Initial dose 2 g Calcid per m³.

shows at least two distinct peaks. A possible explanation of this was given on page 122.

The extent of the differences found in the levels of the gas concentration depends on losses which are increased by circulation and which, apart from the sorbing capacity of the chamber, may be related to the fact that the walls are more or less porous (A. B. P. PAGE and O. F. LUBATTI, 1933).

The great difference found in fig. 7 leads us to infer that a considerable part of the gas penetrates into the plastered walls during circulation. To test this inference gas experiments were carried out in an empty room of 60 m³. The walls of this chamber were covered with oil paint so as to prevent penetration by the gas.

This fumigation was carried out with 2 grams of Calcid per m³. Date of fumigation 4-7-1956. Temperature 18½–19° C. Capacity circulation system: 2400 m³ per hour.

The gas concentrations were determined simultaneously at two different altitudes, viz. 0.20 and 2.00 metres above the floor. The levels of the gas concentration are given in fig. 10. The graph shows that the concentrations (0.72, 0.62 grams of hydrocyanic acid without circulation and 0.55 grams with) in this chamber, respectively with and without circulation differ less than in fumigation chamber A (fig. 7).

From these observations we may conclude that circulation of the gas mixture can cause a quicker liberation of the gas (figures 8 and 9). Circulation ultimately brings about a higher penetration and sorption as a result of which the measured concentration of the free gas is lower after some time than when there is no circulation. Furthermore circulation causes a greater loss of gas when the walls of the fumigation room are porous than when they are coated with paint.

To obtain a good control it is important for the gas penetration of the plant material to be as high as possible. In fact the efficacy of the fumigation depends on the quantity of gas penetrating. As circulation stimulates penetration it is advisable to circulate the gas mixture during fumigation.

On the other hand it is necessary to take care that no losses occur through porous walls, leakage, etc. Coating plastered walls with paint is therefore absolutely necessary in rooms where the gas mixture is circulated.

Discussion

As appears from the preceding chapters the levels of the concentration of the fumigant in the gas phase depends on the following factors:

a sorption by the plants and packing material (dependent on the quantities fumigated);
b sorption by the walls and any scaffoldings in the fumigation chamber;
c circulation of the gas mixture in connection with losses from leakage and porous walls.

Consequently it is impossible to give a general prescription for the dose without taking these factors into account. It is, in fact, no use to state that a dose of 6 grams of hydrocyanic acid per m^3 during a certain time is necessary for the control of the San José scale, or that 18 grams of hydrocyanic acid per m^3 will be necessary for the control of larvae of the large narcissus fly (*Lampetia equestris* F.).

The experiments show that it is possible that sorption has such an unfavourable influence that insufficient control results. According to Beran (1955) a concentration of about 2—2.2 grams of free HCN per m^3 for half an hour is necessary to kill the San José scale. According to our own observations (p. 118) such a consideration cannot be reached, despite the fact that 6 grams of HCN per m^3 are applied, when, for example, there is a large quantity of straw (as packing material) in the chamber. Apart from sorption, straw can prevent penetration of the gas (p. 120).

The experiments in bulb storehouses in particular showed how great an influence the construction and the coating of the walls can have on the levels of the gas concentration. In a well-sealed empty storehouse A without circulation the concentration of the free HCN was 53% of the initial dose two hours after dosing. In a not so well-sealed empty storehouse B this percentage was 9.5 and 0.2 respectively during two tests. When the gas mixture was circulated in the empty storehouse A, which had porous walls, this percentage was about 5 two hours after dosing. In another empty room, the walls of which were covered with oil paint, the percentage was about 65.

These examples show that merely to specify the initial dose (as has hitherto been customary) is insufficient and may lead to entirely wrong results.

To overcome these difficulties two methods may be adopted:

1 the use of uniform fumigation chambers with similar wall coating and the use of the same quantities of fumigation material at all times.
2 the use of the C.T.-product (product of the concentration of free gas and time) as a fumigation characteristic.

It is clear that item 1 is impossible to realize. Nevertheless it is undoubtedly important, especially on an international scale, to aim at the greatest possible uniformity of fumigation chambers. This could be partly obtained by recommending that walls of rooms in which quarantine fumigations are carried out should be coated with oil paint. On addition the rooms should be permitted a certain maximum leakage only (CHISHOLM and KOBLITSKY, 1945).

Apart from this, however, there is still the changing influence of sorption of the commodity and any packing material. To eliminate these effects it is advisable to use the C.T.-products, which should be determined internationally for the various pests to be controlled.

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