

## NEW TECHNIQUES IN FUMIGATION RESEARCH TODAY

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### Abstract

Fumigation with highly diffusive gases is still the most common procedure to kill pest arthropods and vertebrates in agricultural products, in empty and loaded stores, mills and food- and feed-processing factories. Toxic fumigants are also applied in sea going ships and in large churches to control insect pests in the cargo or in the wood.

Mainly due to safety and resistance problems, the stream of research and new developments leads to the less hazardous alternatives and procedures to reduce the risk for workers and neighbours. This has to be done without endangering the high effectivity of toxic fumigants.

For example :

1. Improving the gas tightness and thereby reducing gas loss
2. Reducing the dose due to less leakage or longer exposure
3. Changing the release rate of phosphine from formulations
4. Using filters or catalysts to prevent pollution and make working with toxic gases less risky
5. Replacing toxic gases by modified atmospheres like
  - a) carbon dioxide mixtures with nitrogen and oxygen (< 6 vol.-%)
  - b) nitrogen rich mixtures with oxygen (< 4 vol.-%)
  - c) carbon dioxide and air under high pressure (>10 bar)

The last method excludes any residue problem and reduces the health risk. Solutions 5a) and 5b) can only be applied economically with gas tight enclosures and without restriction in time (sometimes weeks) for the treatment. The use of carbon dioxide under high pressure offers complete pest control within minutes or a few hours!

Safety aspects and new developments are discussed in detail.

### Introduction

Fumigation with toxic gases like phosphine, methyl bromide and hydrogen cyanide is world wide still the most commonly used and efficient practice to control stored product pest insects in large bulks, stacks and/or buildings.

To some extent and under certain circumstances modified atmospheres (reduced content of oxygen, increased nitrogen and/or

carbon dioxide contents compared with air) are substituting the above mentioned classic fumigants.

What are the essential requirements for the use of fumigants?

- effectivity All pests must be controlled in a relatively short time of exposure due to good penetration through and into the treated product and/or space.
- safety The procedure as a whole has to be safe for personnel, neighbours and the environment. Pollution aspects might be relevant to determine wheather or not fumigation is carried out. Good sealing is the logical and neccessary consequence to reduce the dosage of the chemical and thereby the total amount of pollution. Filters and other measurements might be applied to reduce emission even more.

As of now, there appear to be no real alternatives or substitutes for toxic fumigants. Due to the food hygiene regulations, processed food and commercial raw materials must be free of living insects. This can only be achieved by thorough treatments of large amounts of goods using substances with high penetrability. Protectants like contact insecticides, do not have this quality. Furthermore, they have the disadvantageous effect of leading to more or less persistent residues in the treated goods. Products must be turned over completely. This renders insecticide treatments of stored goods uneconomically. Many health departments pursue the idea of keeping the harvest as free of additional chemicals as possible. Consequently, there should not be any prophylactic treatment, which leaves residues. The more common and more reasonable approach to contact insecticides is, the application **after** infestation. On the other hand, one of the most advantageous aspects of toxic fumigants is the application **without** moving the goods.

This aspect combined with the minute build up of chemical residues is the control of the fumigants.

Harmful effects to the workers and the environment can be avoided if the application is carried out properly and if the modern techniques of sealing, pressure testing, leak detection and filtering are applied.

Consequently, the latest innovations in stored product protection are mainly improvements of safety and a reduction of the use of toxic chemicals.

This article concentrates on the description of recent developments in stored product fumigation. Many of the findings and ideas of earlier authors are still valid and indeed worthwhile to study. Specially the works of Monro(1969) and Bond(1984), the two fumigation specialists who have written the very basic and comprehensive Manual of Fumigation for Insect Control, and Peters(1936 and 1942), who published two remarkable booklets, which already contain most of the questions and also some solutions that are discussed today.

### Toxic Fumigants

#### **Phosphine**

Hydrogen phosphide is quite suitable for stored product insect pest control(Hole et al., 1976), provided, that the above mentioned safety measures are followed. The handling and use of

commercial phosphine releasing products are simple and safe (Reichmuth, 1985 a). The following new developments are currently in progress to improve the application:

1. Formulations are changed to delay the release of phosphine during the first hour after opening a tin of the product (DETIA, Germany; QUICK-PHOS, India). This reduces the exposure of workers during the beginning of the fumigation to a minimum.

2. Other developments include the complete sealing as the first step, checking for tightness as the second and, having achieved the required amount of tightness, the application of the phosphine-releasing product through slits, which are cut in the plastic cover and sealed again, as the third step (PROSANITAS, Germany).

The time for sealing thereby is separated from the beginning of phosphine release, which allows for a thorough seal without time pressure.

3. Another new development leads to the direction of continuous scavenging with  $\text{PH}_3/\text{N}_2$  or  $\text{PH}_3/\text{CO}_2$  mixtures from steel cylinders with  $\text{PH}_3$ -concentrations in the treated product at a rather low level of some  $10 \text{ mg/m}^3$  (CSIRO, Australia, ("SIROFLO"), Winks, 1990; ADAS CSL, U.K., Bell et al., 1990). This is based on and can be supported by findings of Reichmuth (1985 b, 1986), who illustrated that excess phosphine above certain concentrations does not reduce the necessary time of exposure to control insects when compared with constant low concentrations.

Unfortunately, the continuous flow technique also causes continuous pollution of the environment. The emission limit in the Federal Republic of Germany for this compound is  $10 \text{ g/h}$  and/or less than  $1 \text{ mg/m}^3$  (Anonymus, 1986). In Germany such a technique does not meet with these values and thus, has to be modified to reduce the emitted amount.

The transportation and handling of steel cylinders under pressure restricts this technique to only skilled personnel.

On one hand, it may prove problematic to release phosphine from steel cylinders under pressure. Protective additives have to be used to prevent the gas from inflammation when opening the valve. This reduces the amount of phosphine per flask. On the other hand, it is a good approach to simply open the valve for some time for fumigation. It can be stopped immediately whenever desired. The dosing of the fumigant is very convenient. The positive pressure helps to distribute the gas evenly in the bulk.

4. The problem of this previous method of the heavy steel cylinders and the high pressure, under which the phosphine is kept, might be overcome by using a generator which produces phosphine safely out of the conventional or modified phosphide product into phosphine. This can be transported into the infested product or area (CSIRO, DETIA).

5. A new development born out of the necessity to avoid  $\text{PH}_3$ -emission in densely populated areas introduced the use of a catalytic unit (DETIA). This unit reduces the  $\text{PH}_3$  content in air by scavenging the gas mixture through prepared charcoal and turning the  $\text{PH}_3$  catalytically to phosphoric acid ( $\text{H}_3\text{PO}_4$ ), which is then captured in the charcoal zone.

This catalytic unit is built on a van and can be transported to any treated building. It can be used to withdraw gas-air mixtures from a fumigated premise or from around a covered and

PH<sub>3</sub>-fumigated stack within a building during and/or after the actual exposure period.

The development of this unit enables the fumigator to almost completely prevent the emission of phosphine. Whenever the product is enclosed inside a building, the airspace around the fumigated area can be used as buffer volume, which is continuously purged with fresh air from outside. All the gas which is diffusing through the plastic cover of the treated product into the airspace is continuously mixed with air and scavenged through the catalytic unit, where it is transformed into phosphoric acid. The charcoal can be regenerated and used several times.

6. For the treatment of sufficiently gas tight grain silo bins there are techniques available to recirculate the gas (Cook, 1980). The latest development in Germany comprises a long pipe which leads from the top of the bin through the grain, a short pipe which is fixed to the top end of the bin ending above the grain and a fan which is linked to both pipes (DETIA). The phosphine product is introduced into the free airspace above the grain.

So called CARTOX-cells (CARTOX being the name of the mixture: 10% ethylene oxide and 90 % carbon dioxide, which is now banned) containing a system for gas recirculation can as well be used for phosphine treatment of grain. The evolving phosphine is recirculated in intervalls of several hours (Reichmuth, 1983). The strong, explosion protected fan can be used together with an electric clock which starts the fan. After some days, when the phosphine is almost completely released, the recirculation can be stopped.

Thus, under Central European climatic conditions, the time for complete control can be reduced to about four days due to very quick and even gas distribution within the bulk.

7. Instead of using fans there are approaches to add carbon dioxide to phosphine releasing products to enhance the conveying of phosphine in a bulk of product (Carmi et al., 1991, Leesch, 1991). Also perforated pipes have been used in the case of in-transit shipboard fumigations. Under certain circumstances this combination might have potential benefits, even though the additional lethal effect of the added CO<sub>2</sub> seems to be limited to some stages of the insects. Especially pupae of *Sitophilus* showed no increased susceptibility (Desmarchelier and Wohlgenuth, 1984).

### **Methyl bromide**

In the Federal Republic of Germany the treatment of flour mills and food processing factories is the largest field of application of methyl bromide. Bag stack fumigation of various agricultural products like cocoa, beans and dried fruits is the other. Treatment of grain is here not registered. Besides this somehow restricted German practice CH<sub>3</sub>Br is used for fumigation of grain and other products in bulk in many other countries.

The strong tendency to reduce the use and especially the pollution caused by toxic substances also applies for CH<sub>3</sub>Br. Moreover, there is still some suspicion of cancerogenicity when comparing this substance with corresponding compounds like ethylene dibromide or carbon tetrachloride. Some studies state contra arguments and deny this critical quality of methyl bromide (Hubbs, 1986 and Reuzel et al., 1987).

Three new tendencies can be reported for the use of methyl bromide:

1. The combination of methyl bromide and carbon dioxide in grain silo fumigation appears to be promising, as far as better and quicker distribution and insect control is concerned (Calderon and Carmi, 1973, Navarro and Donahaye, 1990). Dry ice and subsequently methyl bromide can be applied to the surface of the grain to achieve quick distribution. Recirculation might be advantageous.

2. The inevitable consequence of increasing public awareness over the use of toxic chemicals forced us to look for modifications for the mill fumigation with methyl bromide. The special pollution problem with this empty space treatment consists in the losses of fumigants through vast areas of more or less leaky walls. In the contrary to stack and bulk fumigation, where it is often possible to enclose the product under roof with gas tight plastic liners and to use the space in the building as buffer (as described above, phosphine 5), this approach is not possible when the fumigant is in direct contact with the outer wall. One of the options to reduce the pollution beside improved sealing (which is very expensive in a 100,000 m<sup>3</sup> premise) is the reduction of the actual concentration within the building during the fumigation. According to Fick's law the concentration gradient is a very important factor for the transport of the fumigant through the wall into the ambient atmosphere. Also sorption and losses through holes by strong winds are determined by the concentration inside a treated building. There are indications that constant concentrations of about 5 g/m<sup>3</sup> methyl bromide are sufficient to kill all stages of insects within about 40 hours at 20 °C (Bell, 1978 and 1988).

Figure 1. contains some mortality data for diapausing pupae of *Ephestia elutella* and resistant *Oryzaephilus surinamensis* as well as *Tribolium confusum* at two temperatures.

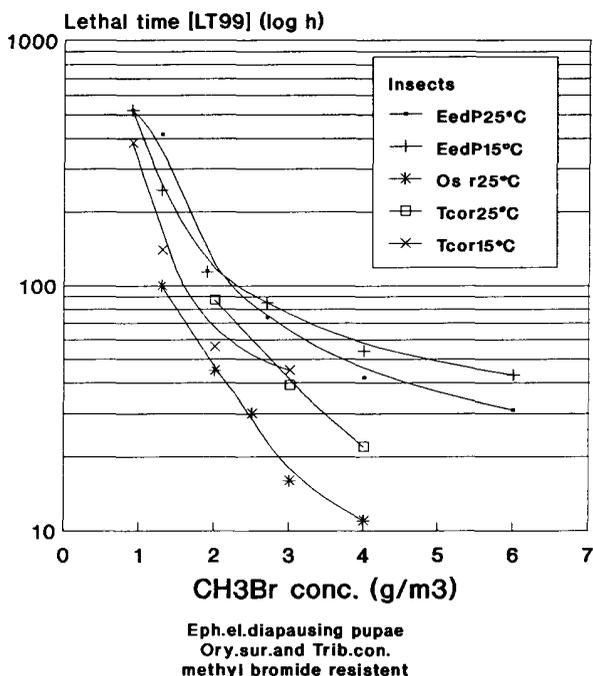


Fig. 1. Methyl bromide efficacy  
Lethal time at 15 °C and 25 °C  
Data of Bell (1978 and 1988)

The target organisms described are presumably the most tolerant against control with CH<sub>3</sub>Br. In practice, probably less methyl bromide or a shorter treatment is sufficient. Even though 5 g/m<sup>3</sup> appear to be a good estimate for about 40 hours.

The usual dose in the Federal Republic of Germany is about 17 g/m<sup>3</sup> methyl bromide. The whole amount is released from cylinders at the beginning of the treatment. This high dose compensates for the losses during the fumigation and is just sufficient for complete control. To guarantee for sufficient toxicant during the end of the exposure time, the concentration has to exceed the necessary (constant) concentration during the first hours of exposure.

If this initial dose is reduced the treatment fails. To compensate for the losses due to leakage, the concentration has alternatively to be kept constant above a low concentration by adding CH<sub>3</sub>Br during the treatment when necessary.

Some laboratory experiments showed the range of concentration being necessary to control the pests.

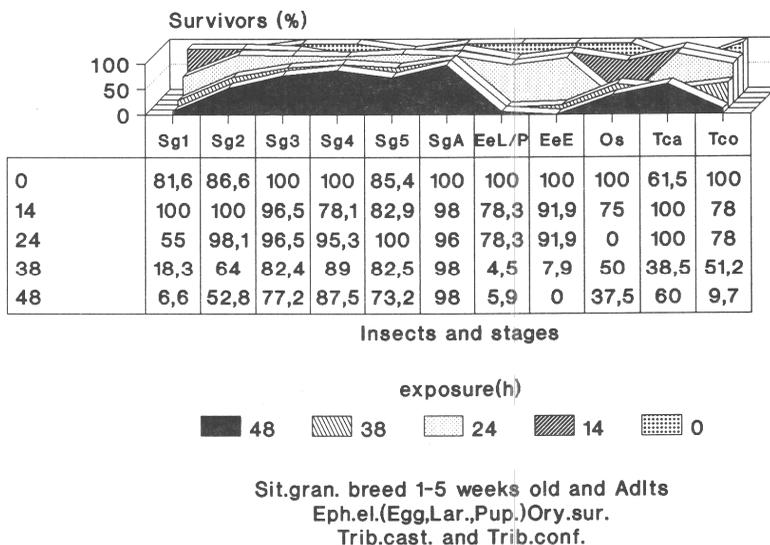


Fig. 2. Methyl bromide fumigation with 2.4 g/m<sup>3</sup> and 3 vol.-% CO<sub>2</sub> at 20 °C

Figure 2. and 3. show results of laboratory experiments in fumigation chambers at 20 °C and 60 % r.h.. All separate stages of *Sitophilus granarius*, eggs, larvae and pupae of *Ephestia elutella*, breed and adults of *Oryzaephilus surinamensis*, *Tribolium castaneum* and *confusum* could not be controlled within 38 hours of exposure to 2.4 g/m<sup>3</sup> CH<sub>3</sub>Br and 3 vol.-% carbon dioxide (fig. 2.). The 100 % kill of *O.s.* after 24 hours was probably an irregular result. Eggs of *S.g.* and *E.e.* are obviously most susceptible and almost complete kill was achieved after 48 hours. 5 g/m<sup>3</sup> CH<sub>3</sub>Br together with 10 vol.-% CO<sub>2</sub> were lethal within 1 day (fig. 3.). No survivors at all were observed after exposures from 24 - 72 hours. Progeny of *T.cast.* in untreated samples was scarce. The results are in good general

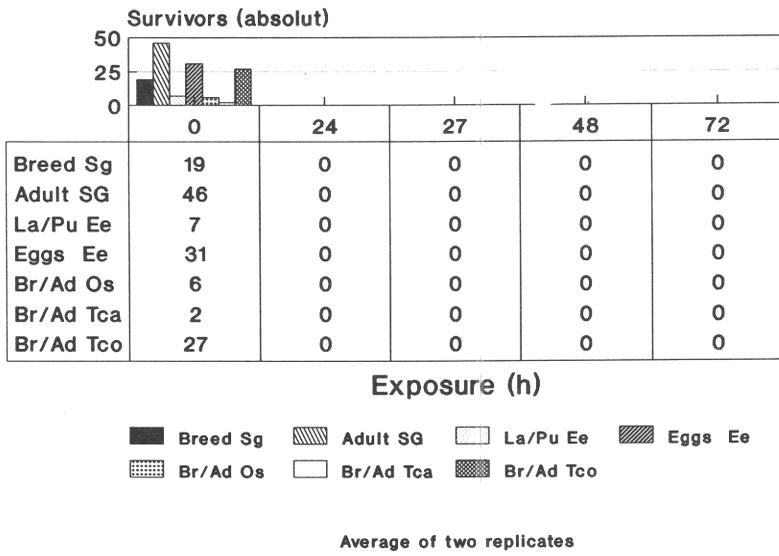


Fig. 3. Methyl bromide fumigation with 5 g/m<sup>3</sup> and 10 vol.-% CO<sub>2</sub> at 20 °C

correspondance with Bell(1988). The CO<sub>2</sub> might have slightly enhanced the mortality. The bromine residues in wheat after this treatment can be expected to be in a fairly low range of about 10 mg/kg with carbon dioxide having no significant effect on the production of residual bromine(Banks and Pinkerton, 1987).

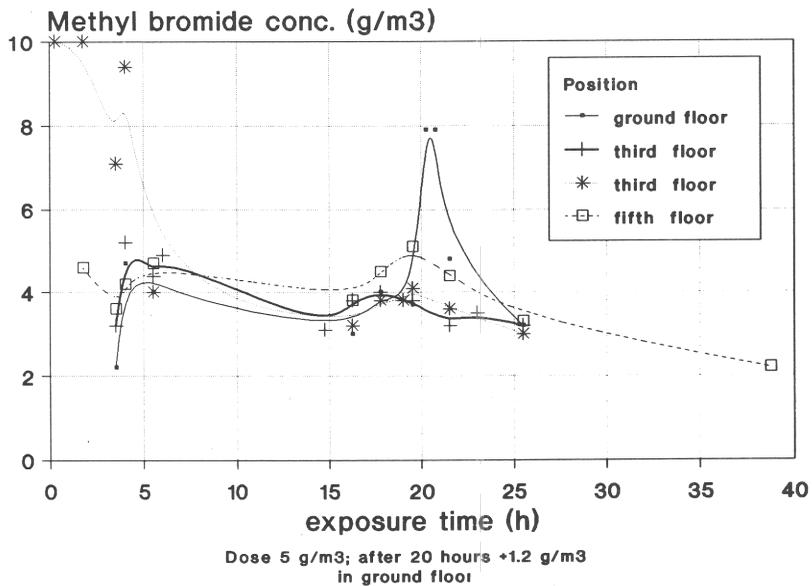


Fig. 4. Methyl bromide fumigation of a flour mill

Results of a field trial in a mill with a volume of about 21,000 m<sup>3</sup> proved the feasibility of the new approach. The CH<sub>3</sub>Br was introduced from steel cylinders on the different floors within the mill. This building was fairly gas tight. Therefore only one addition after 20 hours was necessary to keep the concentration sufficiently high (Figure 4.). It took about 5 hours to obtain even distribution in the mill. The changes after 20 hours can be explained by temperature changes (sunshine!) and the dosing in the ground floor. Altogether 6.2 g/m<sup>3</sup> were used. Additional CH<sub>3</sub>Br was introduced into the ground floor from a cylinder floor by using a pipe and a balance. In other trials also other floors were supplied with long pipes. There are thoughts to use fans in the building to recirculate the fumigant inside to accelerate the distribution. The lethal effect on the test insects was nearly 100 %. Even cockroaches including eggs and adults were controlled completely.

3. Pressure testing is now almost a standard technique in the course of a large scale insect control fumigation in the Federal Republic of Germany. Cheap electronic manometers are now available being suitable to detect pressure differences at a sealed building down to 10 Pa between in- and outside. 10 Pa is in so far reasonable as this is about the natural pressure difference at a building when the wind is blowing with 1-2 m/s. Formulas presented by Banks and Annis(1984) or like :

$$\dot{v} = (a \cdot l) \sqrt[3]{V \Delta p^2} \quad [ 1 ] \quad (\text{Recknagel et al., 1990})$$

with:  $\dot{v}$  = air flow (m<sup>3</sup>/h)

$\Delta p$  = pressure difference (Pa)

$a$  = permeability factor (m<sup>3</sup>/mhPa<sup>2/3</sup>); between 0.1 (tight) and 0.6 (average permeability of a building)

$l$  = length of seam (m) e.g. at a window or door

$V$  = volume of the tested building (m<sup>3</sup>)

try to describe the loss rates from ventilated buildings. [1] is derived from calculations for the necessary heating when buildings are to be ventilated and aerated.

Calculating the distribution of the ventilated gas in the neighbourhood of a fumigated building gave a figure of about:

$$v_{\text{max, tolerable}} = n_{\text{max}} * V = 0.1 * V \quad [ 2 ]$$

with :  $v_{\text{max, tolerable, 10Pa}}$  (m<sup>3</sup>/h) = the maximum gas exchange per hour which can be tolerated without probably exceeding the threshold concentration of 1/20 of the TLV (Threshold Limit Value for workers) of the fumigant around a treated building (distance 10 m or more (Reichmuth and Noack, 1983)) and a pressure difference of 10 Pa. This applies for the whole period of the fumigation including the aeration.

It can easily be seen that this  $v_{\text{max}}$  corresponds to a gas exchange rate  $n_{\text{max}}$ :

$$n_{\text{max}} = 0,1 \text{ (per hour)} = 2.4 \text{ (per day)} \quad [ 3 ]$$

As mentioned, 10 Pa is a quite often in buildings occurring pressure difference in Central European climate. If the wind speed and consequently the pressure difference during the fumigation

is smaller the lossrate from the building will be smaller as well. The transport outside will be more diffusion depending and the mixture with air slower. Due to the reduced pollution rate - compared to the test with 10 Pa - this should not create an immission problem.

In case, that due to higher wind speed the pressure difference is larger, the transport will be intensified but the strong wind outside will provide that the concentrations stay below the threshold. The test is carried out by:

a: either using the appropriate fan which can transport a little bit more than  $v_{\max}$  and measure the pressure difference at  $v_{\max}$  which has to reach at least 10 Pa or

2: by installing a pressure difference of something more than 10 Pa and using a stop watch to measure the half decay time (from 20-10 Pa [or 15-7.5 Pa]).

During this time  $10 \cdot 1 / (100,000)$  [or  $7.5 / (100,000)$ ] parts of the volume of the building have passed. From [ 2 ] it follows that according to the required tightness during 3600 seconds not more than 1/10 of the total volume should be transported through the wall of the building at a pressure difference of 10 Pa. With the assumption that during the decay from 20 Pa to 10 Pa there is at least a driving force of 10 Pa it follows (1 pascal is imposed when the volume is changed by 1/100,000):

$$t_{\min} = [ \{ 10 \cdot 1 / (100,000) \} / 1/10 ] \cdot 3600 = 3.6 \text{ s} \quad [ 4 ]$$

with  $t_{\min}$  being the decay time to achieve the half of an installed pressure difference which should not be smaller than 3.6 seconds.

Off course, this value is not correct because the pressure difference during the decay was greater than 10 Pa as afforded for test 1. A closer figure gives the decay from 15 Pa to 7.5 Pa.:

$$t_{\min} = [ \{ 7.5 \cdot 1 / (100,000) \} / 1/10 ] \cdot 3600 = 2.7 \text{ s}$$

For at least 1/3 of the decay time the pressure difference was less than 10 Pa. Important is here the tendency. In field experiments the author found a good correspondance of about 4 seconds pressure half time and the gas exchange rate  $n = 2.4$ . These values apply for large flour mills of up to 100,000 m<sup>3</sup> which are often very hard to seal.

When a mill passed this test, no real pollution problem was determined later during the fumigation.

## Hydrogen cyanide

The old fumigant hydrogen cyanide which has been used already at the beginning of this century is still the effective gas to control rodents in ships, mills and other food- and feed-processing factories. A survey is given by Reichmuth(1990). As new development it can be reported that now a very sensitive and transportable apparatus is available to detect very low concentrations in air immediately. The detector (HNU, HW 101) is working on the principle of photoionisation. With about

14,000 DM this gear appears to be too expensive for regular use. But taking into account that governmental authorities tend to require certificates of gas concentration measurements around fumigated buildings in critical cases when neighbours might be in danger, this tool is at least cheaper than a whole gas-chromatograph. The results can be recorded. It is very sensitive (detection limit range about 0.01 mg/m<sup>3</sup>) but not specific. For recording concentrations at a fumigation where normally only one compound is used this should be sufficient.

### Carbon dioxide and/ or nitrogen

The subject of the use of inert atmospheres containing high amounts of carbon dioxide and/or nitrogen and low content of oxygen to control stored product pest insects is broadly covered by Banks and Rigby (1991).

In addition to that article only two aspects shall be mentioned:

1. Interest is growing for the use of carbon dioxide under high pressure to disinfect especially high value products like herbs (Stahl et al., 1985, Gerard et al., 1988, Pohlen et al., 1989, Prozell and Reichmuth, 1991). The use of CO<sub>2</sub> is meanwhile registered in the Federal Republic of Germany. The initial investment for the expensive autoclave does not create an obstacle to implement this technique because the short lethal exposure period and the residue free treatment support this approach strongly.

If more than one pressure chamber or a pressure tight charging valve are used the necessary amount of CO<sub>2</sub>/t can considerably be reduced. This can also be done by lowering the pressure according to the time which can be spent for the measure (e.g. during the night)

Figure 5. gives an impression of the required time at different constant high pressures of CO<sub>2</sub> for complete control. The data are derived from Gerard et al. (1988), Stahl et al. (1985), and Prozell and Reichmuth(1991), and field trials.

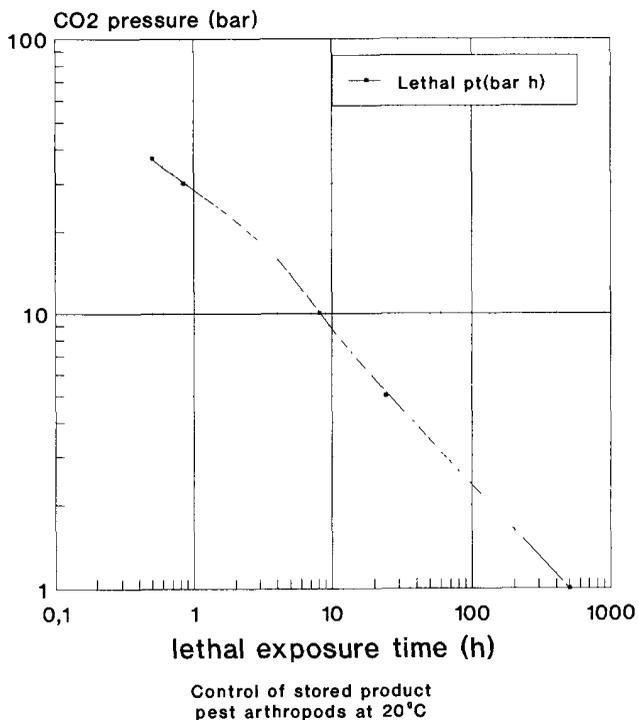


Fig. 5. Lethal exposure time at different CO<sub>2</sub> pressure

World wide there are fumigation chambers available which can now effectively be used for carbon dioxide fumigation.

Provided, gas tightness can be achieved, products which are warmed up are disinfested at slightly reduced or normal pressure within 1 week (30°C) or 1 day (40°C) (Jay, 1986, Reichmuth, 1986, Vail, 1990) (Figure 6.).

2. The experience of silo bin treatment with inert atmospheres enables to give some figures for the expected costs (Love, 1984). Some capital costs are necessary to prepare the bin by improving the gas tightness. The running costs are mainly determined by the degree of gas tightness being achieved in the first step. Sealants and coatings are available which cost between about 1 DM and 20 DM, depending on the treated surface, construction of the building and labour cost (Glet 1984, Newman(1990)).

The costs for the gas are about 0.5 to 1 DM/m<sup>3</sup>, depending mainly on the logistics. The gases are sold by weight, so that 1m<sup>3</sup> N<sub>2</sub> costs about 0.5 DM and 1 m<sup>3</sup> CO<sub>2</sub> about 1 DM.

Figure 7. contains the results of

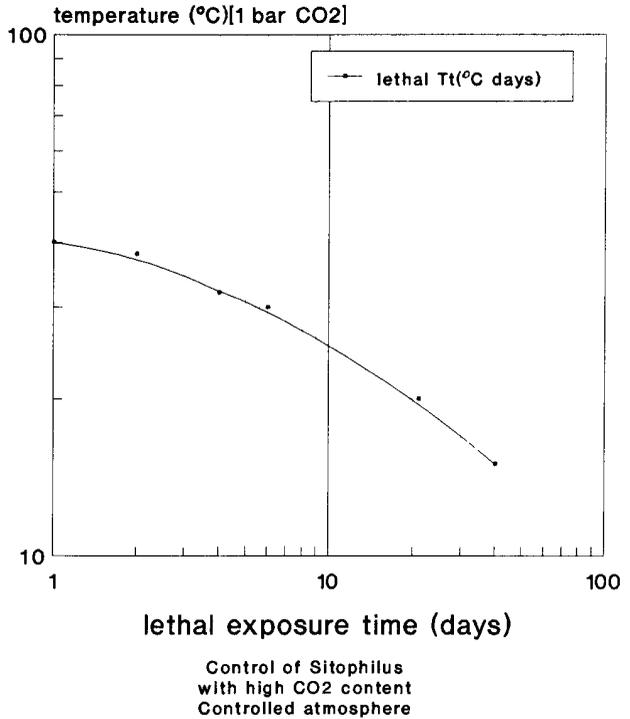


Fig. 6. Lethal exposure time after CO<sub>2</sub> treatment at different temperatures

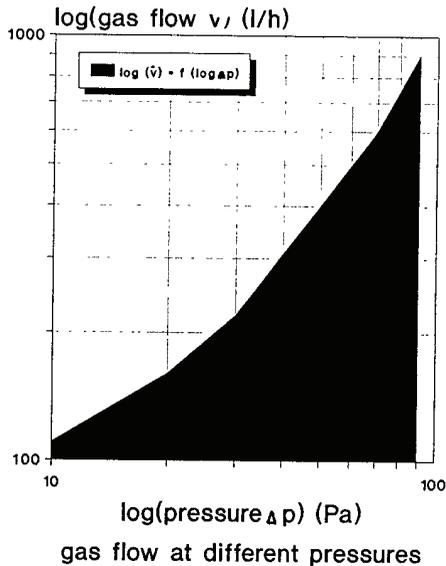
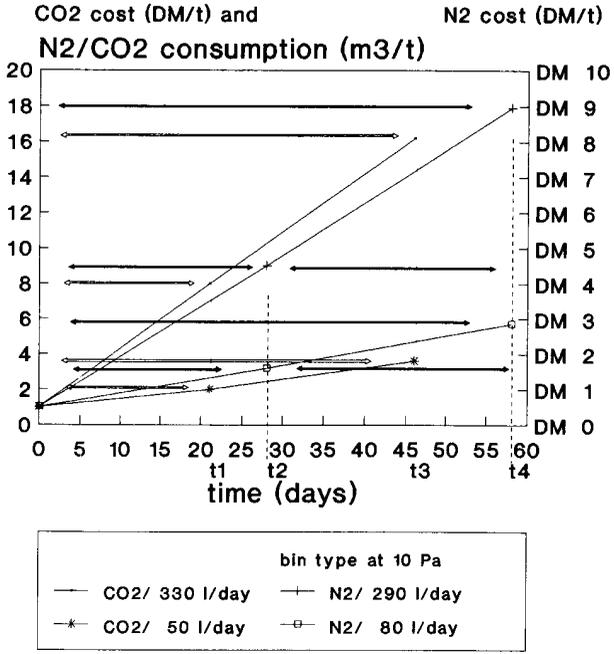


Fig. 7. Pressurs test of a WASTOLAN sealed concrete grain bin

a pressure test with different flow rates from a pressurized grain silo bin which was sealed inside with WASTOLAN (Glet, 1984). The dependency does not follow [1], presumably because the silo bin can not be compared with a building with doors and windows.

Figure 8. reports mainly data of field experiments (Adler and Reichmuth, 1989). It was tried to combine the dependencies of gas consumption, gas tightness and lethal exposure period at two different temperatures and costs for complete control of *Sitophilus granarius* using N<sub>2</sub> or CO<sub>2</sub>. Four types of treatments are described: N<sub>2</sub> and CO<sub>2</sub> in leaky and gas tight bins respectively. Following the initial purge of the gas to replace the air which required about 1 m<sup>3</sup>/t grain of gas in all cases the daily consumption was determined between 50 l/d (CO<sub>2</sub>, tight) and 330 l/d (CO<sub>2</sub>, leaky) with N<sub>2</sub> consumption between.



lethal exposure time:  
 at 20°C: t<sub>1</sub> (CO<sub>2</sub> ) and t<sub>2</sub> (N<sub>2</sub> ) ; N<sub>2</sub> {cost/cons} ←→  
 at 10°C: t<sub>3</sub> (CO<sub>2</sub> ) and t<sub>4</sub> (N<sub>2</sub> ) ; CO<sub>2</sub> {cost/cons} ←→

Fig. 8. N<sub>2</sub> and CO<sub>2</sub> consumptions and costs to control *Sitophilus granarius* at 10°C and 20°C in grain bins with different leakrates

Conclusions

It costs a fortune of several million DM to develop and introduce a new compound and a new control method into the market of stored product protection. On the other hand, the amount of money which can be earned per year in this market is so limited compared for instance with plant protection in the field that the few big special firms are very reluctant to

promote new developments. It has to be repeatedly made clear that this development can be paid off when governments understand that reducing losses **after** harvest should have priority compared with increase of yield in the field **before** harvest. This is also economically the sound approach. But at present, new thoughts are mainly produced by governmental scientists which are more and more under pressure to find private sponsors for realizing their ideas. Thus, the ball is back with the private enterprise.

Another aspect of producing better post harvest situations is the transfer of knowledge and methods to less developed countries in the sense of those countries which lack a certain knowledge. Because stored product pest problems are so similar in all countries it is strongly supported that all responsible bodies act altogether as united human community and work more closer in multinational projects. At present, these possibilities are offered here and there but for some reason this type of cooperation does not work out quite well, the obstacles being mainly the administration. The author wishes to express his hope that this type of approaching mutual problems will be increasingly the way of the future despite the difficulties.

The last years of our century will be marked by the intense search for safer procedures to protect the harvest. The main option will be the modified and safer use of the available (toxic) fumigants and the looking for alternatives like aeration, heat and cold treatment. Very little new compounds ( $O_3$ ??) might be introduced.

Human health and saving the environment will be the main issue. As shown, plenty of good ideas are in the draw to face this demand.

BUSE, FRG, offered facilities to run the  $CO_2$ /high pressure experiments.

DESINSECTA, FRG, supported the methyl bromide experiments.

Dipl. Biol. Mr. H.-B. Detmers performed the  $CH_3Br$  measurements in the flour mill and prepared the graph (fig. 4.). Dipl. Biol. Mr C. Adler is thanked for useful comments on the manuscript.

## References

Adler C. und Reichmuth Ch. (1989) Zur Wirksamkeit von Kohlendioxid bzw. Stickstoff auf verschiedene vorratsschädliche Insekten in Stahl-Getreidesilozellen [Efficacy of  $CO_2$  and  $N_2$  to control various stored product pest insects in grain steel-bins]. Nachrichtenbl. Deut. Pflanzenschutzd. 41, 177-183.

Anonymus (1886) Vorschriften zur Reinhaltung der Luft. Bundesanzeiger Verlagsges. mbH. 38, Köln, FRG, 152p.

Banks H.J. and Annis P.C. (1984) Importance of processes of natural ventilation to fumigation and controlled atmospheres. In: Ripp B.E. et al., ed., Contr. Atm. and Fumigation in Grain Storages, Amsterdam, Elsevier, 75-81.

Banks H.J. and Pinkerton A.(1987)Bromine-containing residues resulting from fumigation of grain with methyl bromide-carbon dioxide mixtures. J. stored Prod. Res. 23, 105-113.

Banks H.J. and Rigby G.R.(1991)Controlled atmosphere storage techniques for grain:the known and the future. These proceedings.

Bell C.H.(1978)Limiting concentrations for fumigation efficiency in the control of insect pests. In: Proc. of the 2<sup>nd</sup> Intern. Work. Conf. on St. Prod. Ent., Ibadan, Nigeria, 182-192.

Bell C.H.(1988)Minimum concentration levels of methyl bromide required for full efficacy against seven species of stored-product beetle at two temperatures. Pestic. Science 24, 97-109.

Bell C.H., Chakrabarti B. and Mills K.A.(1990)Problems and new approaches for the use of phosphine as a grain fumigant in the U.K. In: Fumigation and Contr. Atm. St. of Grain, Champ B.R., Highley E. and Banks H.J., ed., Proc. of an Intern. Conf., Singapore, ACIAR Proc. No. 25, 254-256.

Bond E.J.(1984)Manual of fumigation for insect control. FAO Plant Production and Protection Paper No. 54, 432p.

Calderon M. and Carmi Y.(1973)Fumigation trials with a mixture of methyl bromide and carbon dioxide in vertical bins. J. stored Prod. Res. 8, 315-321 .

Carmi Y., Golany Y., Frandji H. and Segal Z.(1991)Fumigation of a silo bin with a mixture of magnesium phosphide and carbon dioxide by surface application. These proceedings.

Cook J.S.(1980)Low air flow fumigation method. American Patent No. 4,200,657. 8p.

Desmarchelier J.M. and Wohlgemuth R.(1984)Response of several species of insects to mixtures of phosphine and carbon dioxide. In: Ripp B.E. et al.,ed., Contr. Atm. and Fumigation in Grain Storages, Amsterdam, Elsevier, 75-81.

Gerard D., Kraus J., Quirin K.-W. und Wohlgemuth R.(1988) Anwendung von Kohlendioxid unter Druck zur Bekämpfung vorrats-schädlicher Insekten und Milben[Control of stored product insects and mites with CO<sub>2</sub> under pressure]. Pharm. Ind. 50, 1298-1300.

Glet W.(1984)Effective sealants for existing storages from floor to roof. In: Ripp B.E. et al.,ed., Contr. Atm. and Fumigation in Grain Storages, Amsterdam, Elsevier, 159-180.

Hole B.D., Bell C.H., Mills K.A. and Goodship G.(1976)The toxicity of phosphine to all developmental stages of thirteen species of stored product beetles. J. stored Prod. Res. 12, 235-244.

Hubbs A.F.(1986)The subchronic effects of oral methyl bromide administration in the rat. Master Thesis to the faculty of Purdue University.

Jay E.G.(1986)Factors affecting the use of carbon dioxide for treating raw and processed agricultural products. In: Proc. of the GASGA Seminar on Fumigation Technology in Developing Countries. Slough, U.K., Overseas Development Administration, Tropical Development and Research Institute. 173-189.

Leesch J.(1991)The effect of low concentrations of carbon dioxide on the penetration of phosphine through wheat. These proceedings.

Love G.(1984)Cost comparison of different insect control measures. In: Controlled Atmosphere Storage of Grain. In: Ripp B.E. et al.,ed., Contr. Atm. and Fumigation in Grain Storages. Amsterdam, Elsevier, 481-487.

Monro H.A.U.(1969)Manual of Fumigation for Insect Control. 2<sup>nd</sup> ed., FAO Agricultural Studies No. 79, 381p.

Navarro S. and Donahaye E.(1990)Generation and application of modified atmospheres and fumigants for the control of storage insects. In: Fumigation and Contr. Atm. St. of Grain, Champ B.R., Highley E. and Banks H.J., ed., Proc. of an Intern. Conf., Singapore, ACIAR Proc. No. 25, 152-165.

Newman C.J.E.(1990)Specification and design of enclosures for gas treatment. In: Fumigation and Contr. Atm. St. of Grain, Champ B.R., Highley E. and Banks H.J., ed., Proc. of an Intern. Conf., Singapore, ACIAR Proc. No. 25, 108-130.

Peters G.(1936)Chemie und Toxikologie der Schädlingbekämpfung. Sammlung chemische-technischer Vorträge, Neue Folge No. 31, Verlag Ferdinand Enke, Stuttgart.

Peters G.(1942)Die hochwirksamen Gase und Dämpfe in der Schädlingbekämpfung. Sammlung chemische-technischer Vorträge, Neue Folge No. 47a, Verlag Ferdinand Enke, Stuttgart.

Pohlen W., Rau G. und Finkenzeller E.(1989)Erste praktische Erfahrungen mit einem Verfahren zur Druckentwesung mit Kohlendioxid[Initial experience with CO<sub>2</sub> pressure disinfection]. Pharm. Ind. 51,917-918.

Prozell S. and Reichmuth Ch.(1991)Response of the granary weevil *Sitophilus granarius* to modified atmospheres under high pressure. These Proceedings.

Recknagel H., Sprenger E. und Hönnmann W.(1990)Taschenbuch für Heizung und Klimatechnik. 65.Ausgabe, 1766 p. Oldenbourg Verlag, München und Wien, 767, 774-779.

Reichmuth Ch. und Noack S.(1983)Zur Beurteilung der Umweltverträglichkeit von Begasungsverfahren im Vorratsschutz[Judging the impact of stored product fumigation on the environment]. Getreide, Mehl und Brot 37 139-144.

Reichmuth Ch.(1983)Silozellenbegasung mit Phosphorwasserstoff aus Beutelrollen (Bag Blankets)[Silo bin fumigation with phosphine from bag blankets]. Mühle und Mischfüttertechnik 38, 503-504.

Reichmuth Ch.(1985 a)Phosphorwasserstoffbegasung - Neue Aspekte im Vorratsschutz[New aspects of phosphine fumigation in stored product protection]. Gesunde Pflanzen 37, 417-420.

Reichmuth Ch.(1985 b)Zur Wirkung zeitlich nicht konstanter Phosphorwasserstoffkonzentrationen auf den Kornkäfer *Sitophilus granarius*(L.)(Col.,Curculionidae)[Response of the granary weevil *Sitophilus granarius* (L.) to gradually increasing and decreasing phosphine concentrations]. Anz. Schädlingskde., Pflanzenschutz und Umweltschutz 58, 101-106.

Reichmuth Ch.(1986)The significance of changing concentrations in toxicity of phosphine. In: Proc. of the GASGA Seminar on Fumigation Technology in Developing Countries. Slough, U.K., Overseas Development Administration, Tropical Development and Research Institute. 88-98.

Reichmuth Ch.(1987)Low oxygen content to control stored product insects. In: Proc. of the 4<sup>th</sup> Intern. Work. Conf. on St.-Prod. Prot., Tel Aviv, Israel, 194-207.

Reichmuth Ch.(1990)Toxic gas treatment responses of insect pests of stored products and impact on the environment. In: Fumigation and Contr. Atm. St. of Grain, Champ B.R., Highley E. and Banks H.J., ed., Proc. of an Intern. Conf., Singapore, ACIAR Proc. No. 25, 56-69.

Reuzel P.G.J., Kuper C.F., Dreef-van der Meulen H.C. and Hollanders V.M.H.(1987)Chronic (29-month) inhalation toxicity and carcinogenicity study of methyl bromide in rats. Netherlands Organization for Applied Scientific Research (TNO), Report No. V86.469/221044, 31p.

Stahl E., Rau G. und Adolphi H.(1985)Entwesung von Drogen durch Kohlendioxid-Druckbehandlung (PEX-Verfahren)[Disinfestation of drugs by CO<sub>2</sub>-pressure treatment]. Pharm. Ind. 47, 528-530.

Vail R., Buckley M. and Paolocci L.(1990)Modified atmospheres combined with elevated temperatures - fumigation alternative. Association of Operative Millers-Bulletin, 5671-5675.

Winks R.G.(1990)Recent developments in fumigation technology, with emphasis on phosphine. In: Fumigation and Contr. Atm. St. of Grain, Champ B.R., Highley E. and Banks H.J., ed., Proc. of an Intern. Conf., Singapore, ACIAR Proc. No. 25, 144-151.

## LES NOUVELLES TECHNIQUES DE FUMIGATION

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### RESUME

La fumigation à l'aide de gaz à diffusion élevée reste le procédé le plus commun pour tuer les arthropodes et les vertébrés ravageurs de produits agricoles, les magasins vides et les entrepôts de stockage dans les moulins et les usines alimentaire. Les fumigants toxiques sont également employés dans les cargos et les vastes édifices afin de tuer les insectes parasites du grain et du bois. En partie pour des questions de sécurité, et en raison du problème de la résistance, les principales recherches actuelles ont conduit à des solutions moins dangereuses et des procédés nouveaux qui réduiront les risques encourus par les travailleurs et le voisinage. Ceci doit pouvoir être fait sans perdre l'efficacité des fumigants pour l'élimination des ravageurs en contrôlant mieux leur utilisation. Il faut notamment :

- 1) Améliorer l'étanchéité en éliminant les fuites de gaz.
- 2) Réduire les doses en réduisant les fuites et en augmentant les durées d'exposition.
- 3) Changer la vitesse d'hydrolyse des formules de phosphine.
- 4) Utiliser des filtres ou des catalyseurs pour éviter les pollutions et rendre moins risqué le travail en atmosphère gazeuse.
- 5) Remplacer les gaz toxiques par des atmosphères modifiée qui excluent les problèmes de résidus et les risques pour la santé comme : 5a) mélange de dioxyde de carbone et d'azote pauvre en oxygène (< 6 %) ; 5b) mélange riche en azote avec peu d'oxygène (< 4 %) 5c) dioxyde de carbone et air à haute pression (> 10 bars). La solution 5 ne peut être mise en oeuvre que dans des enceintes étanches et selon la température sans restriction de temps (souvent des semences). L'utilisation du dioxyde de carbone à haute pression permet une élimination totale des ravageurs en quelques minutes ou en quelques heures ! Les différents aspects de la sécurité et des nouvelles percées technologiques sont discutés en détail.