THESE recommendations for good fumigation practice were drawn up under the supervision of a working party sponsored by the ASEAN Food Handling Bureau and the Australian Centre for International Agricultural Research. The working party was made up of specialists from the main agencies concerned with fumigation of grain in all countries in the region.

The recommendations are aimed primarily at fumigation of grain and related commodities held in some form of central storage. They provide for the minimum standards that must be achieved if fumigations are to be successful and reliable. The standards are based on a level of sealing of the enclosure, whether it be a permanent structure or a sheeted stack, that will allow pressure testing for gastightness. While this technology may not be immediately applicable, an interim compromise is embodied in the recommendations relying on good construction of the fumigation enclosure and monitoring of gas concentrations during fumigation.

Part 1 of the recommendations lays down the principles and general practices essential for effective fumigation. Parts 2 onward give detailed operational procedures for particular types of fumigations.

" ASEAN-COFAF SUB-COMMITTEE ON FOOD HANDLING "

AFHB

ACIAR

Suggested Recommendations for the

Fumigation of Grain in the ASEAN Region

Part 1

PRINCIPLES AND GENERAL PRACTICE

SUGGESTED RECOMMENDATIONS FOR THE FUMIGATION OF GRAIN IN THE ASEAN REGION

Part 1. Principles and General Practice

ASEAN Food Handling Bureau, Kuala Lumpur
Australian Centre for International Agricultural Research, Canberra

July 1989

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Preface

The development of integrated methods of pest control has been given a high priority by the countries of the ASEAN region because of the serious losses that occur regularly in grain storage. Such management of pests by control measures combining physical approaches with judicious use of fumigants and residual pesticides is a common objective of many development activities of organisations vested with responsibility for care and running of grain storages.

Appropriate use of chemicals in ASEAN was discussed at an international seminar on 'Pesticides and Humid Tropical Grain Storage Systems' sponsored jointly by ACIAR, the Philippines National Post Harvest Institute for Research and Extension, and the ASEAN Food Handling Bureau, and held in Manila in May 1985. During these discussions considerable concern was expressed at the problems associated with fumigation, particularly with phosphine, and at the likelihood of fumigant resistance appearing in the region. Reference was made to the situation already occurring in other parts of the world where high levels of resistance to phosphine have been generated in a range of pest species as a result of inadequate fumigation practice. Concern was also expressed at the actual losses currently occurring from bad fumigations. The point was made by many speakers that immediate action was necessary to avert these serious problems escalating in the region.

These comments were formulated into a recommendation from the seminar that a working party be established, with ACIAR support, to draft for the region a suggested set of guidelines for fumigation that would include dose rates, exposure times, and requirements for gastightness of enclosures. The recommendation was supported by all participants in the seminar and ACIAR agreed to convene such a working party, provided this action had the support of the appropriate organisations in the ASEAN countries.

The proposal for establishing the working party was circulated to:

Indonesia	Chairman, Pesticide Committee Chairman, BULOG
Malaysia	Secretary, Pesticide Board Director-General, LPN Director-General, MARDI
Philippines	Director-General, Ministry of Health Deputy Administrator for Pesticides, FPA Administrator, NFA Executive Director, NAPHIRE
Singapore	Assistant Director, Ministry of Trade and Industry
Thailand	Director-General of Agriculture

as well as to the Acting Team Leader, ASEAN Crops Post-Harvest Programme and to the Director of the ASEAN Food Handling Bureau as co-organiser of the working party.

The proposal had the support of all agencies and, accordingly, the organisers called a meeting of technical personnel from the region and Australia in Singapore in December 1985. At this meeting, terms of reference and a modus operandi were drawn up to enable formulation of the necessary set of recommendations.

The objective of the working party was determined to be:

To develop a viable code of practice and dosage recommendations for fumigation of grain and related products that –

- will ensure high standards of fumigation, both in grain for domestic consumption and for export;
- are appropriate for the ASEAN region, and thus
- reduce losses and spoilage of grain;
- reduce liability of resistance developing;
- minimise residues consistent with good agricultural practice; and
- reduce operator hazards.

The aim of the proposal was to draw up a set of technically sound recommendations that would be available to interested parties in the region. These recommendations would have no official status but would be prepared in such a way that they could be taken by individual countries or organisations and used as the technical basis for appropriate regulations with minimum change necessary. Similarly, they would be suitable for inclusion in commercial contracts or in local operational or training manuals.

A framework was agreed for the suggested set of recommendations and a drafting committee appointed. The draft set of recommendations was discused at a second meeting of the working party, which was held in Kuala Lumpur in October 1987. The draft was revised according to comments from the working party and is presented here.

The recommendations are aimed primarily at fumigation of grain and related commodities held in some form of central storage. Fumigation in farm stores follows the same principles and general procedures but differs in some operational detail.

The recommendations provide for the minimum standards that must be achieved if fumigations are to be successful and reliable. This will reduce loses and prevent development of resistance. If the standards cannot be achieved, fumigation should not be attempted and control of pests should be sought by some other means.

The standards are based on a level of sealing of the enclosure, whether it be a permanent structure or a sheeted stack, that will allow pressure testing for gastightness. It is recognised that this technology may not be immediately applicable and a compromise is embodied in the recommendations relying on good

Membership of the Working Party

Indonesia

- Dr Sadji Partoatmodjo, Chairman, Pesticide Committee
- Dr Mulyo Sidik, Research Co-ordinator, BULOG

Malaysia

- Mr Ramasamy, Pesticide Board, Ministry of Agriculture
- Dr Abdullah bin Abdul Rahman, Ministry of Health

Philippines

- Mr Oscar Angeles, Bureau of Plant Industry
- Mrs Pura Buenaflor, Chief, Standards and Quality Assurance Division, Technical Research and Extension Directorate, National Food Authority
- Mrs Filipinas Caliboso, Head, Food Protection Division, National Post Harvest Institute for Research and Extension
- Ms Perlina Sayaboc, Food Protection Division, National Post Harvest Institute for Research and Extension

Singapore

- Dr Ho Shuit Hung, Department of Zoology, National University of Singapore

Thailand

- Mr Chamlong Chettanachitara, Agricultural Researcher, Agricultural Regulatory Division, Department of Agriculture
- Mr Chuwit Sukprakarn, Storage Entomologist, Entomology and Zoology Division, Department of Agriculture

Personnel that were concerned with developing similar recommendations in Australia:

- Dr H.J. Banks, Senior Principal Research Scientist, Stored Grain Research Laboratory, CSIRO Division of Entomology
- Dr R.G. Winks, Principal Research Scientist, Stored Grain Research Laboratory, CSIRO Division of Entomology

Honorary consultant:

- Mr J.T. Snelson, formerly Pesticides Co-ordinator, Australian Department of Primary Industry

Research leaders and personnel of relevant ACIAR projects:

Long-Term Storage of Grain under Plastic Covers

- Mr P.C. Annis, Senior Experimental Scientist, Stored Grain Research Laboratory, CSIRO Division of Entomology
- Mr J. van S. Graver, Experimental Scientist, Stored Grain Research Laboratory, CSIRO Division of Entomology

Integrated Use of Pesticides in Grain Storage in the Humid Tropics

- Dr M. Bengston, Director, Entomology Branch, Queensland Department of Primary Industries

ASEAN Food Handling Bureau:

- Mr R. Gonzalez, Officer-in-Charge
- Mr J.P. Mercader, Project Officer

ASEAN Crops Post-Harvest Programme:

- Mr R.L. Semple, Technical Team Member

ACIAR Grain Storage Research Program:

- Dr B.R. Champ, Coordinator
- Mr E. Highley, Communications Consultant

construction of the fumigation enclosure and monitoring of gas concentrations during fumigation. The compromise should be seen as an interim measure only, the eventual goal being to pressure test all enclosures before fumigation.

Section A of this first part of the recommendations contains a summary of current knowledge and how it can be applied to achieve successful fumigations. The information presented provides an explanation of the processes involved and justification for the various procedures recommended, so that those responsible for fumigation understand what is involved and why they are doing it.

Section B outlines the various considerations that must be taken into account in deciding whether fumigation is feasible and commercially desirable.

Sections C and D comprise a description of general fumigation procedures and codes of practice for use of particular fumigants. They outline definitively the processes and procedures of fumigation in a format appropriate and with sufficient technical detail for inclusion in official regulations.

Detailed operational procedures for specific types of fumigations are being prepared as a series of separate parts.

'Suggested Recommendations for the Fumigation of Grain in the ASEAN Region' is consistent with Australian Standard AS 2476–1981—covering general fumigation procedures—which may serve as a useful national model. Also, various international organisations, in particular the Food and Agriculture Organization (FAO) of the United Nations, are active in promoting safe and effective use of pesticides. The recommendations have been drawn up in general compliance with FAO's 'International Code of Conduct on the Distribution and Use of Pesticides', details of which are given in the bibliography. Also listed in the bibliography are other publications that may be useful to those seeking to establish a sound regulatory infrastructure for the use of fumigants and other pesticides.

SECTION A. An Introduction to Fumigation Practice

A.1. The Process of Fumigation

In a fumigation, a gas is added to an enclosure for the purpose of controlling or eliminating undesirable organisms. The organisms may be pests of various types—such as insects, rodents, mites, and birds—or microorganisms, or particular plants or seeds. The enclosure can be made from a diverse range of materials, including metal, concrete, bricks, mud, and plaster, and various plastic membranes. It is necessary to contain the fumigant gas while it acts on the target organisms and to restrict its escape into areas where it may be dangerous to human health. All commonly used fumigants can be dangerous at concentrations more dilute than normally used in fumigation.

A fumigation is a complex process. Efficient fumigations can be carried out only by properly equipped and trained personnel in appropriately prepared fumigation enclosures. Stringent safety precautions are required. At present many fumigations are carried out poorly. Such treatments can be both dangerous and expensive without being effective. The treated commodities can be tainted or otherwise adversely affected and the development of resistance (tolerance) to the fumigant may be encouraged.

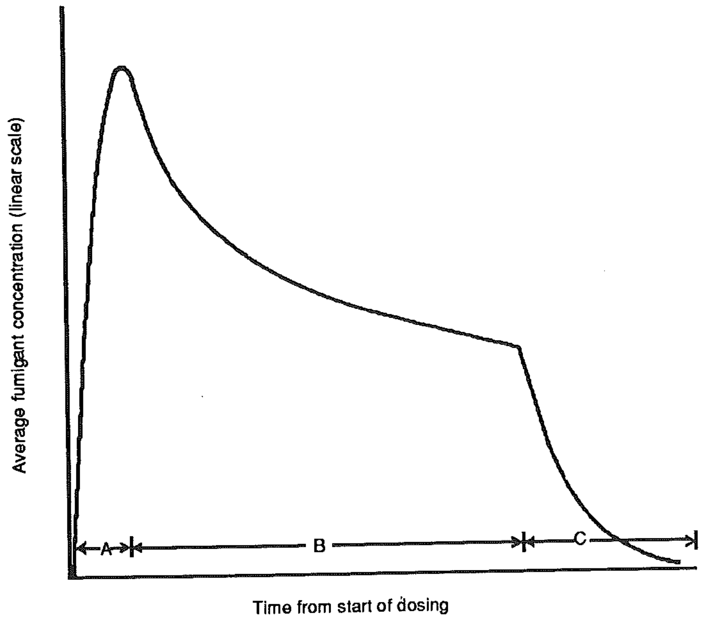
These notes set out guidelines for the conduct of good fumigations in the ASEAN region. They also provide background details of the physical, chemical, and biological processes involved in fumigation. An understanding of these processes is important to those involved in fumigation. It provides reasons why treatments succeed or fail, why particular actions are recommended *even though they may require extra effort or cost or delay,* and when fumigations are or are not appropriate.

A.2. Background to Effective Fumigation

All fumigants are, by definition, gases. They are subject to various simple laws describing their action on biological organisms, their interaction with commodities, the way that they are dispersed within a fumigation, and how they leak or are forced from an enclosure. It is important to understand these laws in order to be able to perform fumigations safely and effectively. In particular, it is essential to be aware of the various forces acting on gases within an enclosure and how these influence gas concentrations over time.

Figure A1 shows a generalised time course for a fumigation. There is an initial generation phase where the toxic atmosphere is formed, a decay phase where the concentration of fumigant drops slowly over the exposure period, and a ventilation phase where the fumigant is removed after the necessary dosage has been achieved.

Fig. A1. Generalised time course for a fumigation, showing the changes in gas concentration during the three phases of a typical fumigation: A, fumigant introduction; B, exposure period; and C, ventilation period.



The generation phase may take from only a few minutes to hours or several days, depending on the fumigant used. Similarly, the decay and ventilation phases may vary from a few hours to many days.

In a fumigation, it is the intention to maintain a certain level of gas for a sufficient period to effect control of the pests within the fumigation enclosure. The dosage or **Ct** (concentration × time) product achieved in a particular situation for a given quantity of fumigant is largely determined by the rate of loss of fumigant during the decay phase. If there is no fumigant added to the enclosure during this phase, the concentration, C, decays exponentially with time, **t**, according to the equations:

$$C = C_0 e^{-k(t - t_0)} \quad (1)$$

or

$$\ln C_0 - \ln C = k(t - t_0) \quad (2)$$

where **C** is the concentration at any time **t**, C_0 is the concentration at time t_0, **k** is the decay rate constant in units of [time^{-1}], such as 'per day', and e is the base of natural logarithms. The value of **k** can be found from the slope of the semilogarithmic graph of concentration against time. For most fumigations, this graph will be linear during most of the exposure period under constant environmental conditions (Fig. A2) and, in many cases, after an initial more rapid fall, a similar semilogarithmic relationship is found for the ventilation phase.

The value of the decay rate constant, **k**, is influenced by a number of different factors. Consideration of the magnitude of the contributions of these factors leads to an explanation of why, in practice, fumigations are often partially successful and to guidance on how to avoid a poor fumigation treatment. The observed value of **k** can be used as indication of how well a fumigation was carried out. It is independent of the size of the enclosure.

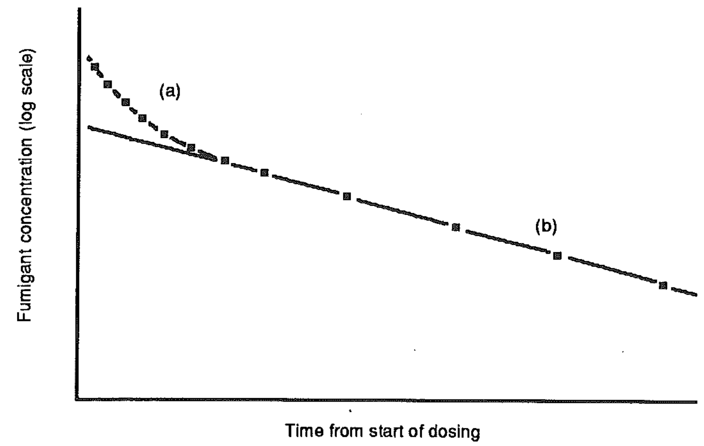


Fig. A2. Typical variation of fumigant concentration in a treatment during the exposure period, showing (a) an initial rapid fall in concentration, and (b) a slow semilogarithmic loss.

The value of **k** can be broken down into contributions from environmental forces (**k'**), sorption (**k"**), and permeation (**k"'**). The overall decay rate constant is then given approximately by **k = k' + k" + k"'**. The magnitudes of these contributions vary with different situations and fumigants. In very leaky enclosures, environmental forces may be the main cause of gas loss and thus the main contributors to **k**. Sorption effects predominate in well-sealed enclosures with most fumigants. Permeation is an important contributor only with very small enclosures, e.g. 1 kg plastic packs, or with certain building materials, e.g. hardboards.

For fumigant loss to occur as a result of any of these factors, a gradient in concentration of fumigant must be present. This is the normal situation in a fumigation. The gradient can be in the form of a difference in concentration inside and outside an individual grain, leading to sorption phenomena; a reaction within a grain removing fumigant and leading to a lowered local concentration; a difference across a permeable membrane leading to permeation loss; or a difference across a leak resulting in the escape of fumigant from the enclosure.

A.3. Properties of Commonly Used Fumigants

Basic physicochemical properties of the fumigants phosphine (PH_3), methyl bromide (CH_3Br), carbon dioxide (CO_2), and hydrogen cyanide (HCN) are given in Table A1.

It will be noted that carbon dioxide and phosphine are gases at temperatures much below those normally encountered while methyl bromide and hydrogen cyanide boil above 0°C. Carbon dioxide and methyl bromide are substantially more dense than air. Phosphine is flammable at a low concentration and hydrogen cyanide is very soluble (miscible) with water.

A.4. Choosing the Correct Fumigant

The choice of fumigant will depend on an evaluation of a number of factors, including:

- the time available
- the commodity to be fumigated
- the cost and ease of application

- possible reaction with non-target material
- operational considerations
- market requirements and residue limits.

A.4.1. Time Available

In general, there are three factors involved in determining the time needed to complete a successful fumigation:

- the time required for the fumigant to disperse throughout the fumigation enclosure, either by natural means or by forced distribution;
- the exposure period required after the fumigant has been dispersed throughout the commodity, which is a function of time and the intrinsic toxicity of each fumigant; and
- the time required to clear fumigant from the commodity at the end of the exposure period.

Each of these three components varies with the choice of fumigant, the method of application and distribution, and whether ventilation is achieved by natural means or by forced draught. For example, if the time available for fumigation is short, fumigants requiring long exposure periods—such as carbon dioxide and phosphine—would be unsuitable. Only methyl bromide or hydrogen cyanide may be used in such circumstances. On the other hand, the slow desorption of methyl bromide and hydrogen cyanide from treated commodities increases the total time required for fumigation with these gas and needs to be allowed for in the fumigation schedule.

Table A1. Properties of common fumigants

	Phosphine	Methyl bromide	Carbon dioxide	Hydrogen cyanide
Formula	PH_3	CH_3Br	CO_2	HCN
Molecular weight	34	95	44	27
Boiling point (°C)	−87.0	3.6	−78.5	25.7
Specific gravity (gas) (air = 1.0)	1.2	3.3	2.0	0.9
Vapour pressure at 30°C (atm)	42	2.5	71	1.2
Conversion factor g/m^3 to ppm (30°C, 1 atm)	730	260	560	890
Flammability limits in air (v/v)	>1.7%	13.5–14.5%	nonflammable	6–46%
Solubility in water (v/v)	0.2	3.4	0.76	Highly soluble
Specific gravity at 30°C, (liquid, kg/L)		1.7	0.93	0.69

A.4.2. The Commodity

The most important consideration in selecting a fumigant is likely to be its effect on the commodity, since this will be, in the majority of cases, a food destined for human consumption. Fumigants may react with commodities to produce unacceptable residues. Alternatively, reaction with or sorption by the commodity may be sufficient to seriously reduce the concentration of fumigant available to act on infesting insects, so reducing the efficacy of the treatment. In cases where seed for planting is to be fumigated, phytotoxicity (toxicity to plants and plant parts) must also be considered.

A.4.3. Cost and Ease of Application

When assessing the relative costs of fumigants the following components need to be considered:

- the cost of the chemical or formulation
- the cost of getting it to the fumigation site
- relative costs of delays and other arrangements associated with specified exposure and airing periods
- the cost of equipment and personnel needed to introduce the fumigant into — and remove it from — the fumigation enclosure
- the cost of security during the fumigation and for safety equipment such as gas masks and detector tubes
- the cost of special equipment such as vaporisers
- cost of disposal, or return, of empty containers and cylinders.

Also, the costs of any extra sealing of the enclosure need to be taken into account.

A.4.4. Reactions with Non-target Material

In some situations the choice of fumigant may be influenced by the possibility of it reacting with other materials in the fumigation enclosure. For example, phosphine attacks copper and copper-containing alloys and therefore poses a risk to electrical and electronic equipment. Methyl bromide attacks natural rubber and other compounds containing free sulfur groups; it also attacks aluminium. Carbon dioxide reacts with alkaline substrates such as new concrete. Hydrogen cyanide dissolves easily in free water. Reaction with non-target materials may be important because of the damage caused or because of the loss of available fumigant.

A.4.5. Operational Considerations

The choice of fumigant may also be influenced by operational factors such as:

- the time available to provide grain or other commodity for a particular shipment
- whether a storage complex can continue to function while fumigation is in progress

- whether the commodity needs to be moved to permit introduction of fumigant or to ensure its distribution
- whether it is permissible to vent the fumigant of choice into the local environment around the treatment.

A.4.6. Market Requirements

Where a commodity is to be exported, there may be requirements of the importing country to consider. For example, quarantine laws in some countries may require that commodities be fumigated with a particular chemical such as methyl bromide. It will be necessary to take into account maximum residue limits when they are imposed by the importer. For example, inorganic bromide levels following fumigation with methyl bromide may present problems with some commodities.

A.5. Effects of Fumigants on Commodity Quality

Fumigants, by their chemical nature, are reactive chemicals. They can have unwanted and adverse effects on the treated commodity. It is essential to be aware of these effects when choosing a fumigant for a particular situation. Unfortunately, very little specific information is available on this subject for the hot, humid storage conditions encountered in the ASEAN region.

Fumigants can affect:

- germination, seedling vigour and dormancy
- organoleptic (taste, appearance, and texture) qualities
- processing parameters
- mould growth and mycotoxin formation.

Residues of unchanged fumigant may persist for long periods in a commodity. Fixed residues, resulting from chemical reaction of constituents of the treated commodity or air with the fumigant, can also be produced.

Residue limits (mg/kg) for fumigants*

Phosphine	0.03 as phosphine
Methyl bromide	50 as bromide ion
Carbon dioxide	No limit
Hydrogen cyanide	75 as cyanide ion

*Maximum level permitted in raw cereal grains by Codex Alimentarius (1987).

Though it may be considered that any adverse effect of fumigation is to be avoided, the magnitude of these effects on the commodity should be kept in perspective. A heavy insect infestation, if not controlled, may cause substantial direct losses and may also lead to loss of quality through moulding and moisture migration, contamination of the product with insect fragments, excreta, and other materials

such as quinones, and loss of germinability both through direct feeding on the germ and the adverse storage conditions produced by the infestation. The detrimental effects, even of a reactive fumigant such as methyl bromide, may be small compared with the effects of an unchecked infestation.

A.5.1. Effect on Germination Parameters

For stored grains, such as seeds for planting or malting barley, in which effects on the performance of the grain as a plant are important, three effects of fumigants can be distinguished. These are:

- loss of germination;
- loss of vigour and harvest yield of the resulting seedlings; and
- effects on dormancy and rate of germination.

A.5.1.1. Loss of Germination

Many compounds used as fumigants in the past have adverse effects on germination. Ethylene oxide, in particular, causes severe loss of germination. Chloropicrin and, to a lesser extent, methyl bromide, also cause loss of germination. These effects are enhanced by high moisture content in the treated grain, long exposure times, high grain temperatures, high dosages, or multiple applications. Indeed, most of the factors which enhance fumigant toxicity against the target insects also increase their detrimental effects on germination. The detrimental effects may be delayed and become more apparent after a period of storage subsequent to treatment.

Most fumigants are significantly phytotoxic. Phosphine, carbon dioxide, and hydrogen cyanide are virtually without effect on germination. They should be considered for use whenever germination of the treated grain is important. However, even these fumigants may produce some adverse effects on particular cultivars of grain or under special circumstances. For instance, loss of germination of one Egyptian wheat variety has been found after phosphine treatment. Some maize cultivars appear to be very sensitive to fumigants. When possible, local varieties should be checked for sensitivity to fumigants before large quantities are treated.

A.5.1.2. Seedling Vigour

In tests of the effects of fumigants, the effect on the vigour of the seedlings produced from treated seeds is seldom considered. Nevertheless, it is an important aspect of the overall phytotoxicity of fumigants since it has a bearing on susceptibility to adverse conditions (drought, disease, etc.) and affects final yield.

Even the least phytotoxic fumigants may have a slight effect. Phosphine treatment, for instance, has been found to reduce the vigour of seedlings from a hybrid white maize variety, a particularly susceptible plant and strain, and also to reduce the final yield. Where a fumigant has a slight effect on germination, its action may be more pronounced on seedling vigour and yield. This should be borne in mind when treating sensitive seeds.

A.5.1.3. Dormancy

Some seeds require a length of time to elapse after ripening even though conditions are otherwise apparently favourable for germination. This phenomenon is known as dormancy. Few studies have been performed on the effect on dormancy of the fumigants normally used in stored grain disinfestation. Hydrogen cyanide can catalyse breaking of dormancy in barley. Data on rice dormancy are notably lacking.

A.5.2. Organoleptic Effects

Several fumigants will cause unusual smells or effects in raw cereal grains if they have been insufficiently aired after fumigation. The more highly sorbed and odorous gases, e.g. hydrogen cyanide, are prone to this. Odours may also result from incomplete decomposition of solid fumigant formulations such as aluminium phosphide or calcium cyanide. The residual unchanged material from these formulations may decompose when a fumigated grain stock is moved or milled. The small quantities of fumigant liberated give a smell which may be unfamiliar to those handling the grain.

Methyl bromide can cause taint on both flour and whole grain if applied incorrectly. In particular, contact with liquid methyl bromide or excessive treatment will taint flour, presumably from formation of volatile sulphur compounds through reaction with sulphur-containing grain constituents. Slight 'staleness' has been found in freshly baked bread rolls from flour of wheat which has undergone multiple methyl bromide fumigations. Wrapping of bread made from flour fumigated with methyl bromide may help retain the smell that can be detected in freshly baked loaves. Soybean flour should not be treated with methyl bromide as it is particularly susceptible to persistent taint.

A.5.3. Effects on Processing Qualities

Remarkably little work has been done on the changes induced by fumigation on the processing and handling properties of treated grain and data on tropical grains and products derived from them are notably lacking. However, all fumigants so far investigated have been shown to alter the baking properties of flour derived from treated wheat and some effects may be expected with other products.

A.5.4. Mould Growth and Toxin Formation

Fumigants can alter the rate of mould growth and toxin (mycotoxin) formation, both directly by effect on the mould and indirectly by restricting mould growth. Fumigation appears to be generally, but not always, beneficial (i.e. it reduces mycotoxin production). For instance, formation of aflatoxin (a carcinogenic mycotoxin) may be increased by phosphine in some *Aspergillus* strains. Little is known on this subject.

A.6. Residues

Fumigants are sorbed by treated commodities. At the end of a treatment, fumigant in the gas phase is removed from the enclosure by natural or forced ventilation. Fumigant desorbing from the commodity is also removed. However, some

unchanged but sorbed fumigant may remain as residue. The quantity remaining depends on environmental factors, the nature and condition of the treated commodity, and the kind and quantity of fumigant applied.

Some fumigants (e.g. methyl bromide, phosphine) react or decompose during a treatment, giving various fixed residues and sometimes materials derived by chemical combination between the fumigant and some constituent of the commodity.

Both fixed and unchanged fumigant residues may have regulatory limits set on their quantity in foodstuffs, restricting their use and sometimes requiring action to minimise their development. Details of the levels and types of residues are given in **Section D**, where the individual fumigants are discussed.

A.7. Estimation and Detection of Fumigants

In a well-conducted fumigation the fumigant concentration achieved within the enclosure is measured from time to time during the exposure period. Fumigant concentration should be monitored in workspaces close to enclosures under gas. After a fumigation it is necessary to check that the fumigant has been aired off adequately. It may also be necessary to check residue levels in the treated commodity. The information on fumigant concentrations during a treatment provides a check on whether the intended dosage and distribution were, in fact, achieved. The other data are required for safety and sometimes for legal or contractual reasons.

Industrial hygiene standards for worker exposure to fumigants have been established. These are based on a time weighted average concentration for a normal 8-hour workday and a 40-hour workweek, to which all workers may be repeatedly exposed, day after day, without adverse effect.

Daily Threshold Limit Values–Time Weighted Averages (TLV–TWA)*

	ppm (v/v)	g/m^3
Phosphine	0.3	0.0004
Methyl bromide	5	0.019
Carbon dioxide	5000	8.7
Hydrogen cyanide	10†	0.011

*American Conference of Governmental Industrial Hygienists 1988
†Ceiling limit that should not be exceeded during any part of the working exposure

The concentration to which workers can be exposed continuously for a short period of time without suffering from (1) irritation, (2) chronic or irreversible tissue damage, or (3) narcosis of sufficient degree to increase the likelihood of accidental injury, impair self rescue, or materially reduce work efficiency—*provided that the daily TLV–TWA is not exceeded*—is defined as the Threshold Limit Value–Short Term Exposure Limit (TLV–STEL).

A Short Term Exposure Limit is defined as a 15 minute time weighted average exposure which should not be exceeded at any time during a workday, *even if the 8-hour time weighted average is within the TLV. Short term exposures should exceed three times the TLV–TWA for no more than a total of 30 minutes during a workday and UNDER NO CIRCUMSTANCES should they exceed five times the TLV–TWA provided that the TLV–STEL is not exceeded.*

The apparatus needed for estimation and detection of fumigants varies with the fumigant used and the situation. The accuracy and precision of analysis required also varies. Details of the apparatus required for particular fumigants are given in **Section D**.

In general there are three distinct analytical problems to be faced:

1. Estimation of fumigant at insecticidal concentrations under field conditions.
2. Detection and estimation of fumigants in the region of the health limit concentration in the field.
3. Analysis of fumigant residues in the laboratory.

Accuracy of ± 20% may be acceptable for monitoring progress of fumigations and for safety monitoring but ± 5% can be needed for residue determinations.

Some of the apparatus required is both expensive and complex. It is essential that the apparatus be properly maintained and used by well-trained and reliable persons. Though the problems of fumigant estimation are undoubtedly substantial, contributing to the cost and organisational difficulties of a fumigation, they nevertheless must be faced if treatments are to be done safely and if confidence is to be placed in the results.

A.8. Environmental Effects

The component of the overall decay rate constant resulting from environmental effects is given by

$$\mathbf{k'} = \mathbf{Q}/\mathbf{V} \tag{3}$$

where **Q** is the volumetric rate of flow of gas (leakage) from the enclosure of gas volume, **V**. Thus, by minimising **Q**, the leakage value, **k'** (see **Section A.2**), is minimised for a given situation. **Q** is related to the pressure difference, **Δp**, across the leaks in the fabric and the flow characteristics of leaks, defined by the empirical parameters, **b** and **m**, in the equation

$$\mathbf{Q} = \mathbf{b}\Delta \mathbf{p}^{\mathbf{m}} \tag{4}$$

where **b** is a measure of leak size for a given value of **m**.

In general, 0.5 < **m** < 1.0. Sealing decreases the value of **b**, and thus the value of **Q** and **k'**, over a given period. This mathematical analysis is the logical basis of why a fumigation enclosure must be sealed. It will also be noted that when gas removal is required at the end of a fumigation, opening the enclosure maximises **Q**, by increasing **b** for a given **Δp**, and thus maximises **k'**.

In approximate order of importance, the environmental effects which influence the value of **k** (the overall decay rate constant) are:

- wind
- stack effect
- temperature variation
- pressure variation.

The actual contribution of each individual factor will vary with circumstances (fumigant, type of enclosure, sealing level, etc.). Although not strictly additive, the contribution of each factor may be considered in isolation.

It can be shown theoretically that, for a good fumigation, the total decay rate constant from environmental effects should be less than 0.10 per day.

A.8.1. Wind

For leaky fumigation enclosures, such as often are used in practice at present, the main cause of gas loss, and thus fumigation failure, is wind. Wind causes increased pressure on the windward faces of an enclosure and decreased pressure over the rest of the enclosure. Wind will force air into the enclosure if **Δp** > 0 at a leak. A vacuum there (**Δp** < 0) will tend to withdraw fumigant. Where there are several leaks, these effects may act in concert causing a flow of air into the enclosure at some places and loss of fumigant at others. The rate of loss of fumigant will be approximately proportional to wind speed and, for leaky structures under windy conditions, may often be so fast that a fumigation is made ineffective because the toxic gas is removed before an adequate **Ct** product has been achieved.

For wind to cause rapid gas loss, it is necessary to have two holes in the enclosure, an air entry and a gas exit. With only one significant hole wind will still cause some losses, through pressure fluctuations (see **Section A.8.2**), but its effect is much reduced. Sealing of an enclosure reduces the effect of wind dramatically. While in a poorly sealed enclosure values of **k'** of greater than 10 per day, particularly for small enclosures, may often occur under windy conditions, enclosures sealed to an adequate standard for good fumigation practice (see below) will have **k'** less than 0.05 per day under the same conditions. Indeed, the main effect of sealing a fumigation enclosure, is the reduction of the loss from wind and the stack effect (see **Section A.8.2**) to an insignificant level. During the ventilation phase of a fumigation, where gas loss is to be maximised, wind or a forced draught are the most effective means of dispersing the fumigant.

A.8.2. The Stack Effect

The 'stack' or 'chimney' effect is the name given to the force causing gas loss generated when the atmosphere within the enclosure and the one outside differ in density. This density difference causes pressure differentials across the enclosure walls, so that the pressure inside the enclosure (ρ_{int}) differs from the pressure outside the enclosure (ρ_{ext}) and, if these occur where there are leaks, as with wind, a flow-through of gases results (see Fig. A3).

For a flow to occur, there must be a vertical distribution of leaks. The density difference can result from either temperature differences or differences in composition between the atmosphere within and outside the enclosure.

Because the pressure differential created is dependent on the height of the enclosure and the leakage produced is proportional to the pressure differential, the stack effect is much more important in tall enclosures, such as silos, under fumigation than with squat ones. In most cases, wind-caused losses are much greater than those from the stack effect. This is to be expected, as both vary with general 'leakiness' but the pressures produced by wind are usually much greater than those from the stack effect.

Except under windless conditions and in tall structures, it is unlikely that the stack effect alone will cause fumigation failure throughout an enclosure by giving rise to excessive gas loss. However, it can result in localised regions of inadequate exposure where air is brought into the enclosure, diluting the fumigant to ineffective levels. Survival of pests in these 'havens' may result in a resurgence of infestation after treatment.

A.8.3. Temperature Variation

When the temperature of the gases within a fumigation enclosure changes, the pressure within also changes. In a leaky enclosure, if the pressure rises because of heating, gas is forced out and if it falls, through cooling, air is drawn in. Note that only heating is of relevance to the fumigant loss rate. When air is drawn in, the average fumigant concentration remains constant in terms of grams per cubic metre within the enclosure.

Temperatures in the headspace (the free space between the top of the grain and the roof) of a storage may vary substantially during a fumigation, giving rise to loss rate constants of up to 0.05 per day in extreme cases. For fumigations which are completed in less than a day, such a rate is tolerable overall but for those requiring several days exposure period, notably phosphine, precautions must be taken to reduce this rate to less than about 0.02 per day. This corresponds to an average daily temperature variation in the enclosure of 6°C. Temperature variation can be minimised by ensuring that the enclosure is as full as possible with commodity, as the temperature within a commodity bulk varies very little on a daily basis. For

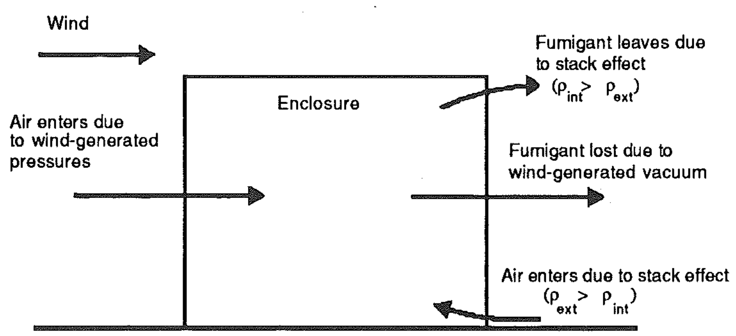


Fig. A3. Gas loss caused by wind and the stack effect from a partially sealed enclosure.

galvanised iron structures, it is beneficial to paint the outside with a white, heat-reflectant paint. This treatment markedly reduces absorption of solar radiation and thus heat gain by the gases within the enclosure during the day. Insulation or shading of the roof is also helpful. Note that because the pressures generated by daily temperature variation are maintained over a long period (some hours in a fully sealed system), their contribution to gas loss cannot be reduced by sealing, except at an impracticably high level. In an imperfectly sealed system, the long time over which the force acts ensures that pressure equilibrium is attained across the enclosure wall and the full rate of gas loss expected from the variation is attained. However, a high level of sealing may reduce the contribution of short term variations, e.g. over a few minutes.

A.8.4. Atmospheric Pressure Variations

The atmospheric pressure varies on both a daily (tidal) and long term basis. A drop in atmospheric pressure results in a pressure difference across an enclosure wall tending to withdraw gas from the enclosure. The contribution to the overall rate of gas loss from this change is generally small, less than 0.01 per day, and can usually be neglected. This loss cannot be prevented except by a very high level of sealing, not achievable in practice.

In the special case where an enclosure, such as a container or rail wagon, is fumigated in transit, pressure variation may be a significant cause of gas loss. Whenever the enclosure is raised, such as by ascending a hill, the external pressure falls and gas is lost. A rate of ascent of 3000 m per day, a reasonable rate over mountainous terrain, will give a loss rate constant of about 0.4 per day.

A.9. Sorption–Desorption Effects

All fumigants are, to some extent, sorbed by commodities. The rate of sorption is dependent primarily on the fumigant itself and the commodity fumigated, but is also influenced by prevailing temperature and humidity. Most fumigants appear to be sorbed at a rate approximately proportional to their concentration in the gas phase, at least in the first few hours of a fumigation. Mathematically, this implies that they follow a decay consistent with equations (1) and (2) (**Section A.2**). Some fumigants are sorbed reversibly (e.g. carbon dioxide), while others, at least in part, are sorbed irreversibly (e.g. hydrogen cyanide, methyl bromide, phosphine). Irreversible sorption implies that the material reacts chemically with the commodity.

In most cases, the total quantity of fumigant which can be sorbed increases with molecular weight and boiling point. Hydrogen cyanide is exceptional because, although relatively volatile and of low molecular weight, it is very water-soluble and thus highly sorbed. If sorption is reversible, the desorption rate decreases with molecular weight. Thus, relatively non-volatile fumigants such as chloropicrin or ethylene dibromide are easily sorbed and to a high level, but are slow to air off after a fumigation compared with low molecular weight fumigants such as phosphine and carbon dioxide. In practice, the effects of sorption can be illustrated by the quantity of fumigant penetrating into a bag of a sorptive material in a given time. The proportion of fumigant penetrating a bag of flour as a function of boiling point is given in Figure A.4.

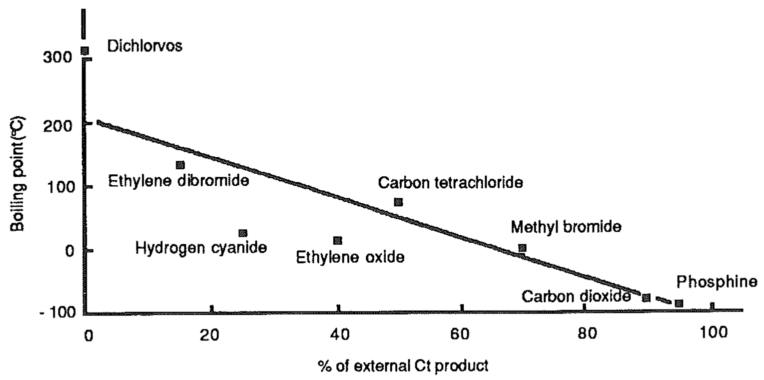


Fig. A4. Ct products achieved at the centre of a 63 kg bag of wheat flour, for different fumigants, as a percentage of the external Ct product [redrawn after Heuser (1975)].

There is a complex interaction between sorption and temperature. In general, the quantity of fumigant physically sorbed decreases with temperature, though equilibrium is reached more rapidly. Where there is also chemisorption, the overall effect of temperature may be increased sorption at higher temperatures as these usually increase the velocity of the reaction. Where equilibrium chemical reactions are involved, high temperatures may either increase or decrease the quantity of sorbed fumigant depending on the thermodynamics of the process involved.

The apparent loss rate of fumigant from an enclosure as a result of sorption, **k"**, is dependent on the filling ratio, **f**, where the filling ratio is defined as the ratio between the volume actually occupied by the commodity and the total enclosure volume. (Note that in many cases a storage is full to normal capacity yet the commodity bulk may only occupy a small fraction of the total space. In such cases, **f** is less than 1.0 and may even be less than 0.5 despite the storage being 'full'.) The observed decay constant, **k"**, of fumigant is related to the decay constant appropriate to a completely filled system, k_{full}, (**f** = 1.0) by the equation

$$k'' = f\, k_{full} \qquad (5)$$

The rate of loss from sorption is independent of leakage from the enclosure. In many situations, and particularly those in which the enclosure is sufficiently sealed to eliminate significant wind effects, it is the dominant mode of gas loss. Thus, in a well-conducted fumigation, the overall loss rate will approach that expected from sorption only.

Fumigant that has been taken up by a commodity either reacts to form fixed residues or is capable of being desorbed again. The rate of desorption is controlled by the diffusion rate of the fumigant within the grain particle, how long the particle has been exposed to fumigant and thus whether the fumigant has penetrated far into the particle, the chemical and physical interactions between the fumigant and commodity, and the fumigant concentration external to the particle. During forced venting of fumigant this concentration is kept close to zero. The desorption rate is then controlled solely by diffusional movement within the particle and will be independent of air velocity over the particle and thus of speed of forced ventilation.

A.10. Permeation and Diffusion Losses

The process of permeation involves the transfer of fumigant molecules through an intact material such as a fumigation sheet. No imperfections or leaks are required for this process to occur. The rate depends on the fumigant used and its concentration, ambient temperature, and on the thickness and type of film. Diffusion is the process of transfer of fumigant over distance simply through the motion of individual molecules. No bulk movement of gas occurs. For diffusion to cause leakage, there must be a leak in the fumigation enclosure. The molecular motion then transfers fumigant through this leak.

In practice, the contribution of **diffusion** to the overall leakage rate is generally negligible, as it is usually overshadowed by the other, more powerful factors causing gas loss (see **Section A.8**).

Generally, the contribution of **permeation** to the overall decay rate constant is also negligible, even in enclosures made from light plastic membranes. It may be significant in very small enclosures made of thin films—a few litres capacity or less—with a very high surface-to-volume ratio.

Permeability constants of, for example, PVC (polyvinylchloride) and low density polythene plastic sheeting, are small and give rise to low loss rates of fumigant gases from enclosures of a size typical of general storage practice. The loss rate of methyl bromide from a 100 tonne rice stack held within 0.2 mm PVC has been calculated at 0.06 per day, while the equivalent value computed for phosphine is 0.005.

Loss rate constants through common (porous) building materials are generally orders of magnitude higher than those through the plastic sheeting used for fabrication of fumigation enclosures. This highlights the need for effective sealing of permanent structures before they are fumigated.

A.11. Factors Affecting Local Concentrations of Fumigant within an Enclosure

In a fumigation, it is important not only to achieve a satisfactory average dosage regime, but also to ensure that an adequate regime is attained throughout the enclosure, so that there is no survival of pests after the treatment.

When fumigant is added to an enclosure it is applied in some concentrated form. Mixing of some kind is needed to provide the required uniform concentration of fumigant throughout the enclosure, exposing all parts to the maximum dosage for minimum usage of fumigant. The rate of mixing within the enclosure is determined by four forces: convection, forced mixing, sorption, and diffusion. The last two forces are negligible contributors to overall distribution in large enclosures but may be important in the penetration of caked areas or those containing dust and broken material.

There is an important balance between the rate of mixing within the enclosure and the rate of leakage of air into an enclosure. In **Section A.8**, several forces were considered which can reduce the average fumigant concentration in the gas phase. Many of these—wind, the stack effect, temperature, and pressure variation—were concerned with bulk movement of gases through leaks in the enclosure. The loss of fumigant at one point or time was compensated for by the gain of air into the enclosure at another point or time. When air enters an enclosure under fumigation, it dilutes the fumigant in the region close to the leak. If enough air enters, it may create a region in which the fumigant dosage is locally inadequate, despite an apparently good average concentration. The rate at which fumigant re-enters a region from which it has been removed by incoming air is an important variable in fumigation practice, as it determines the extent of the regions of lowered fumigant concentration under given leakage conditions. High rates of mixing can reduce these havens where pests may survive.

A.11.1. Convection

Convection is the dominant natural process of mixing and gas transfer occurring within most fumigation enclosures, except perhaps in very small or almost isothermal enclosures.

Convective currents are set up within an enclosure by the occurrence of horizontal gas density gradients. These density gradients may result either from temperature or composition differences. The density gradients result in pressures which force the gases to circulate. The convection patterns may involve a large part of the storage in a single circulation system or be restricted to a small region. Strong convective currents may be produced by a warm core in a grain bulk with a cool periphery. Substantial convective forces are often produced by heat of metabolism of pests and moulds.

In many cases under sealed conditions, convective mixing will produce an even distribution of a volatile fumigant, e.g. phosphine, methyl bromide, or hydrogen cyanide, within a day. However, if the enclosure is leaky, convective mixing may not be rapid enough to cope with the rate of air entry through leaks, and forced mixing will be required to achieve the desirable even distribution.

A.11.2. Forced Mixing

In many fumigation procedures, some form of forced mixing is used. This includes specially designed recirculation equipment, such as fitted to some silos, and the use of fans to distribute fumigant in space fumigation of buildings, such as flour mills. Forced mixing is used in situations where natural convection is too slow to give an adequate fumigant distribution and is thus used particularly for short exposures, as with methyl bromide treatments. It is also useful to prevent 'layering', which occurs when a dense fumigant vapour is added to an enclosure without adequate mixing. A layer of dense gas forms at the bottom of the enclosure and this can persist during the exposure period. An apparently similar 'layering' occurs when there is little convective mixing and air is drawn into the top of the enclosure by the stack effect. The denser fumigant is lost from the bottom. Note that once air and fumigant vapours are mixed, they will not separate to produce a layer if they remain as gases, although in extreme cases under low temperatures, there may be condensation of some fumigants and layering could then occur.

A.11.3. Sorption

The rate at which a fumigant moves through a grain bulk is strongly influenced by its sorptive behaviour. This is important both where a given fumigant level is to be achieved for insect control and subsequently when the fumigant is being removed at the end of the exposure. Relatively non-volatile or highly sorbed fumigants will travel less rapidly through a grain mass than the air carrying them. Because the fumigant molecules spend significant time sorbed on the grain during their passage through it, their rate of travel is slowed relative to the air. If a mixture of a more and less volatile fumigant is applied to grain, the materials will travel at different speeds and may even separate completely. With highly sorbed fumigants, convective currents may often be insufficient to give a reasonable fumigant distribution within a bulk in the exposure period allowed, and forced mixing will be required. However, given a high rate of air movement, even the most highly sorbed fumigants can be distributed through grain.

Highly sorbed fumigants take a considerable time to ventilate from grain bulks under natural means, and forced ventilation may be needed to reduce fumigant residues to an acceptable level. Even the most volatile fumigants are retained for substantial periods on grain. The rate of desorption is controlled not only by the rate of air passage through the bulk, but also by the rate of movement of the fumigant to the surface of individual grains and the rate of any reversible chemical reactions which may be retaining fumigant. Thus, after a period of forced ventilation following a fumigation—when the fumigant concentration in the air coming from the grain has reached a low level—if the fan is switched off for a period, more fumigant may desorb from the grain and the fumigant concentration may rise again, sometimes to hazardous levels.

A.11.4. Diffusion

Diffusion is a molecular phenomenon. No bulk gas movement occurs, but the individual fumigant molecules, which are always in thermal motion, disperse from a concentrated to a more dilute system because of their velocity. While diffusion is often believed to be a major cause of fumigant dispersion in an enclosure, it is has a pronounced effect only over distances of less than a few centimetres, and is normally insignificant compared with convective mixing for the distribution of fumigant around a large enclosure. However, diffusion is important in the penetration into packed commodities, after the fumigant has reached the surface of the commodity bulk. The rate of diffusion is inversely related to the molecular weight of the material and in a grain bulk is about one-third of that in air.

A.11.5. Implications of Forces Affecting Gas Loss and Distribution on Enclosure Design

It can be seen that consideration of the various forces affecting gas loss and distribution should have a significant bearing on fumigation practice:

- Sealing is required to prevent gas loss from wind and the stack effect. Gas loss can result in lowered fumigant concentrations in localised regions close to leaks and, in extreme cases, inadequate concentrations overall. It may also be a health hazard.

- To restrict gas loss further, temperature changes should be minimised by painting the enclosure white or by shading, insulating, or thatching.
- Forced distribution may be required with highly sorbed fumigants or when convection currents are too slow to disperse fumigant throughout the enclosure in a time that is short compared with the planned exposure period.
- Tall enclosures, e.g. silo bins, are likely to retain gas less well than squat ones, because of the stack effect.
- It is important not to provide a through path between leaks in an enclosure when gas loss is to be restricted but useful when gas loss is to be encouraged such as on venting after an exposure.
- Care must be taken to ensure that fumigant is fully desorbed after a fumigation.

A.12. Principles of Fumigant Toxicity

A.12.1. Factors Governing the Dosage of a Fumigant

Fumigation as a control technique may be described simply as the establishment of an atmosphere containing a lethal gas in the environment of an insect at a concentration high enough and an exposure period long enough to kill the insect. There is a somewhat arbitrary distinction between the terms dose and dosage. The **dose** may be described as the, frequently unknown, quantity of fumigant absorbed by an insect from its gaseous environment. **Dosage,** on the other hand, refers to the measured amount of fumigant in the environment from which a dose is absorbed during a period of exposure to that environment. It is clear then that the dose absorbed by an insect is a function of the concentration and the time of exposure.

If the dose is a function of both concentration and time, it follows that both may be varied, providing that the combined effect remains the same. Hence, the same effect may be produced by a low concentration for a long time, or a high concentration for a short time. This leads to the familiar relationship between concentration and time, sometimes known as Haber's Rule, which states that the product of concentration and time for a specified level of kill is constant. This may be represented as:

$$\mathbf{C} \times \mathbf{t} = \mathbf{K} \qquad (6)$$

where **C** = concentration, **t** = time of exposure, and **K** is a constant. Unfortunately, this simple relationship is at best an approximation and should be used as a guide to dosages in the field only in those cases where specific recommendations permit its use and only within the upper and lower limits of concentration that are given in the recommendations.

A more general relationship between concentration and time is of the form:

$$\mathbf{C}^{\mathbf{n}} \times \mathbf{t} = \mathbf{K} \qquad (7)$$

where again **K** is a constant equalling the dosage for a specified level of response such as the LD_{99} (the lethal dose for 99% of the pest population present). The

exponent **n** is sometimes known as the toxicity index and is a specific value that describes the toxicity relationship between a fumigant and a species or, to be more exact, a developmental stage of a species. *Its importance to practical fumigations lies simply in knowing the general magnitude of* **n** *for the fumigant being used and the species in question.* For example, the values of **n** for phosphine are mostly less than 1 which indicates that the exposure time is the more important to the outcome of the fumigation than the concentration. Put another way, it is a better strategy with this gas to prolong the fumigation than to increase the concentration. However, to be able to do this the fumigation enclosure must be sufficiently gastight to retain the gas for the longer period or a method of continuously adding fumigant for the required period must be used. With the latter approach a minimum level of gastightness must still be obtained.

For fumigants for which the value of **n** is greater than 1 it would be more effective to increase the concentration than to increase the exposure period. Methyl bromide falls into this category in most cases.

Whichever **Ct** relationship describes the fumigant, it is important to note that it will apply only over a discrete range of concentrations. Therefore, unless the limits of concentrations and times are specified, recommended dosages and times should be strictly adhered to.

A.12.2. Selection for Resistance to Fumigants

Fumigants have been used for many years in most countries for the control of grain pests. They are an important component of insect control strategies and if used correctly provide high levels of kill. Many fumigations are carried out in structures that do not meet an adequate standard of gastightness and, with the consequent high gas loss during the exposure period, survival may occur. This may result in selection of the population for fumigant tolerance and, if fumigation is repeated often enough, resistant populations may emerge.

The number of fumigants acceptable internationally is limited. If a fumigant becomes ineffective because of resistance and an alternative fumigant has to be chosen, it is almost certain that the alternative will—because of lower toxicity to insects or because of residue problems, greater phytotoxicity, or sorption/desorption characteristics—be inferior. For this reason, it is important that the fumigants now in common use be used effectively so that their usefulness will be prolonged. Above all, they should be used only in structures or enclosures that achieve the required standards of gastightness. Secondly, the dosage rates and exposure periods should be chosen carefully and adhered to. Thirdly, a system of monitoring for fumigant resistance should be maintained so that if resistance develops it can be detected quickly and strategies based on reliable information can be developed to control such strains. Control failures may be the result of resistance, but frequently they are caused by poor fumigation practice. It is essential that strategies designed to control fumigant resistant strains are introduced only after it has been established that resistance is the real cause of the control failure. This is particularly relevant at low concentrations. There may be a threshold concentration of fumigant below which the fumigant is ineffective even when an indefinite exposure is applied. At this concentration the target organism is able to detoxify or otherwise cope with the fumigant and thus be unaffected.

Methods for the detection of fumigant resistance in grain pests have been drawn up under the auspices of FAO (FAO 1975). The use of these methods in the ASEAN region is strongly supported. They are reprinted as Appendix 1 of these recommendations.

Alternative fumigants include carbon disulphide, chloropicrin, and ethyl and methyl formate. However, these are currently not widely accepted for disinfestation in international trade and, in many countries, their use is restricted or prohibited by national regulations. Carbon disulphide is a cheap, practical fumigant for the tropics where the high ambient temperatures favour its volatilisation and penetration into commodities. Its high flammability and low flash point are a disadvantage. On the other hand, while it requires relatively large doses for effective fumigation, these do not impair seed viability. Chloropicrin, which is commonly added to methyl bromide and hydrogen cyanide as a warning agent (tear gas), is extremely toxic to insects. It is used as a fumigant on its own, but because of its high boiling temperature is difficult to vaporise. Also, chloropicrin is highly sorbed by commodities, is difficult to air off, and is very phytotoxic. These properties have limited its use as a fumigant. Ethyl and methyl formate are chemicals whose use as fumigants has hitherto been restricted to specific applications, such as fumigation of individual packages of dried fruit.

These chemicals have now largely been superseded by phosphine and methyl bromine. However, their potential as replacement fumigants in the tropics has yet to be fully investigated.

SECTION B. Considerations for Management

Fumigation is a versatile technique that can be applied in a wide range of situations. The details of the procedure required to ensure a successful fumigation vary greatly with different circumstances. There are a number of important generalisations that can be made, however, to help management assess a particular situation and decide what fumigant to use and what preparations and precautions are required to ensure both the safety and efficacy of the process.

Fumigation should be undertaken only when management is satisfied that a need to carry out pest control exists, that fumigation is the appropriate process, and that the fumigation may be safely and effectively carried out. There are several other methods of pest control available and one or more may be preferable in particular circumstances (see **Section B.2**).

Fumigation is a precise operation, requiring considerable expertise and cannot be undertaken without proper preparation. It is important that management realise this, and ensure that due planning is carried out before fumigation is required.

An essential requirement for fumigation is an enclosure that will retain the fumigant at sufficiently high concentrations over the exposure period. Barges and lighters, shipping containers, and whole warehouses or godowns may be used providing they are adequately sealed. Gastight plastic sheeting is used commonly to enclose bag stacked commodities, whereas specially manufactured fumigation chambers may be used in situations where fumigations are regularly carried out. Bulk storages also may be constructed so that they are gastight.

B.1. Is Fumigation Appropriate?

Fumigation is usually the preferred method of pest control in warm and humid climates, where pests must be eliminated without moving the infested commodity. Often, fumigation of commodities in the export trade may be mandatory for quarantine or contractual reasons. Fumigation is useful where a rapid kill of pests is required and for effective removal of pests from structures into which clean commodities are to be brought. In situations where there is a choice between fumigation and use of contact pesticides (e.g. organophosphate compounds, pyrethroids), the residues left by fumigation may be considered more acceptable.

Fumigation must not be used when:

- trained operators are not available;
- the enclosure in which the fumigation is to be carried out cannot be sealed to an adequate standard;
- workers and other persons cannot be reliably excluded from the enclosure and risk area; and

• fumigant cannot be safely aired from the enclosure after the exposure is complete.

Given careful planning before the need for treatment becomes critical, it is possible to meet all the safety and operational requirements of fumigation in almost all situations. However, some actions, e.g. training, storage modification, sheeting of ground beneath stacks may have to be carried out months or even years in advance of the treatment.

It is important that management realises that fumigation may be required and takes the necessary steps well in advance to ensure that fumigation can be carried out safely and effectively. Where management has no expertise in pest control in general, and fumigation in particular, it will be necessary to call for assistance from a qualified and licensed pest control adviser in planning the required operations.

There are special circumstances involved in fumigation of ships. These are covered in two publications of the International Maritime Organization (IMO), details of which are given in the Bibliography.

B.2. The Need for Fumigation and Timing of Treatments

The need for pest control in a given situation is influenced by three main factors:

- acceptability of the observed level of pests;
- suitability of the environment for multiplication of the pests; and
- how long the commodity is to be retained before being passed to control of other parties.

In effect, an assessment must be made whether there is an immediate requirement for control, whether a treatment should be applied to avoid an anticipated pest problem, or whether action is not needed. To make such an assessment an action level needs to be defined. These considerations lead to three possible decisions:

- immediate treatment of an existing problem;
- immediate treatment of an anticipated problem; or
- no action.

B.2.1. Action Levels for Treatment

As a working rule, populations of storage insect pests will multiply 50-fold every 6 weeks under tropical conditions, unless control measures are applied. Thus, an infestation initially at levels low enough to escape detection by normal sampling may quickly build up to damaging and unacceptable proportions. High populations of insect pests not only cause direct losses through their feeding but may cause indirect damage through their production of metabolic heat and moisture that lead to increased moisture migration and production of conditions conducive to moulding.

Thus, if infestable commodities are to be stored for more than about 6 weeks under humid, tropical conditions, a precautionary fumigation is often advisable before infestation becomes obvious and before the infestation sets up conditions that may make subsequent storage difficult.

It follows that pest control treatments are likely to be required whenever commodities are accepted into storage, except when they are to be moved on quickly (within a few weeks), and are already acceptably free of infestation. Any commodity taken in for longer term storage should be treated immediately as it can be assumed that it will have become at least lightly infested in transit and it was probably not stored in insect free conditions previously. Grain may be infested in the field and contaminated with pests from harvesting and handling machinery and during transport. Infested materials brought into store are a potential hazard to disinfested commodities already in store as they provide a source of cross-infestation.

In commercial trade within a country, an infestation level of one live insect per kilo at time of sale can be taken to be the maximum tolerable in human foodstuffs to be consumed soon after purchase. If this standard is to be met, a low level of infestation, less than 20 insects per tonne, is acceptable if 6 or fewer weeks storage remain. Higher levels may be acceptable in human food that will be milled or processed before consumption, e.g. paddy, or for animal foodstuffs.

Export markets may stipulate their own phytosanitary requirements, and a fumigation at export is often required to meet these specifications.

Insect pests may require control where export markets or food standards have specifications for the quantity of insect fragments ('filth') present in a commodity. Only very low levels of infestation can then be tolerated and fumigation is often required to restrict insect proliferation and accumulation of insect fragments.

B.2.2. Choice of Fumigant

Once a decision to fumigate has been made, it is necessary to choose which fumigant to use. Four materials are generally available and approved for use: phosphine, methyl bromide, carbon dioxide, and hydrogen cyanide. Each of these has advantages and disadvantages. The choice will be influenced by six principal factors:

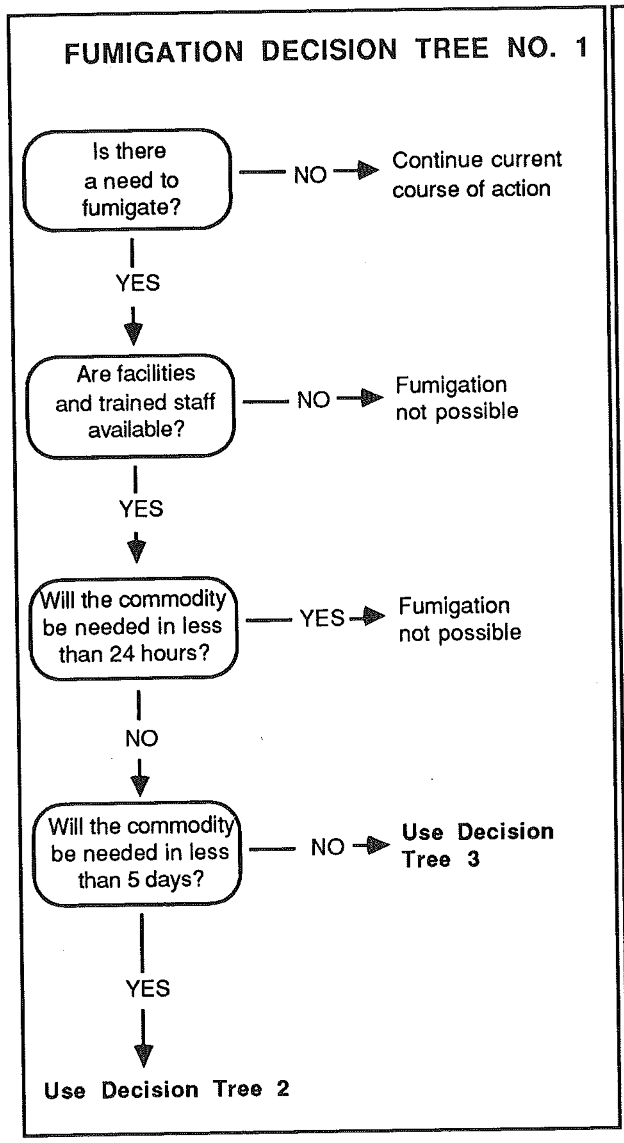
- requirement for short treatment time
- effect of fumigant on the commodity, and existing residue levels
- target organisms
- economic advantages and availability of particular materials
- training of fumigators
- environmental safety considerations.

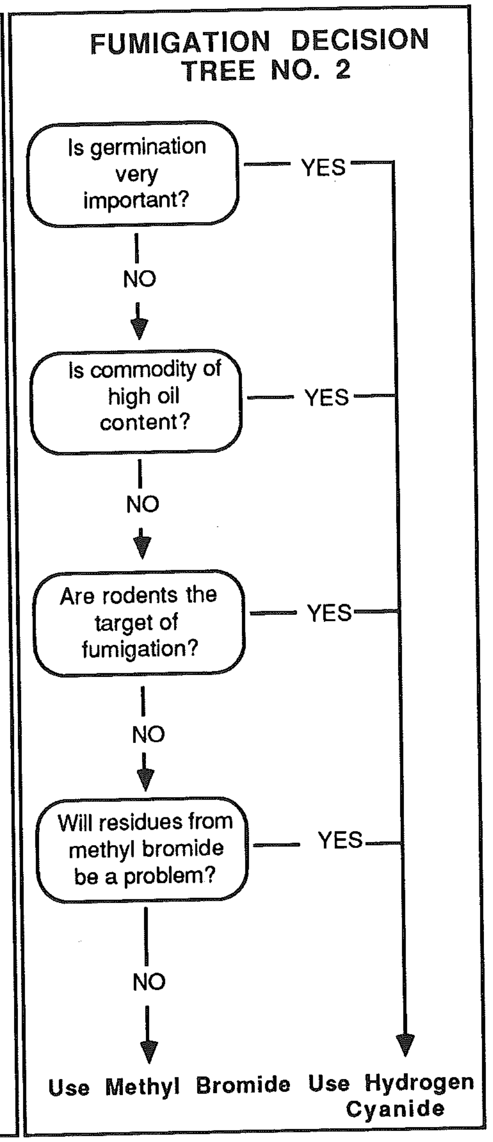
Phosphine and carbon dioxide generally require long exposure periods (7 and 15 days, respectively, under hot tropical conditions), whereas hydrogen cyanide and methyl bromide provide a rapid fumigation that can be completed in less than 4 days, often within 24 hours. The presence or absence of certain tolerant insects may influence both the choice of fumigant and the length of the exposure period. The target organisms may be tolerant and require longer exposure.

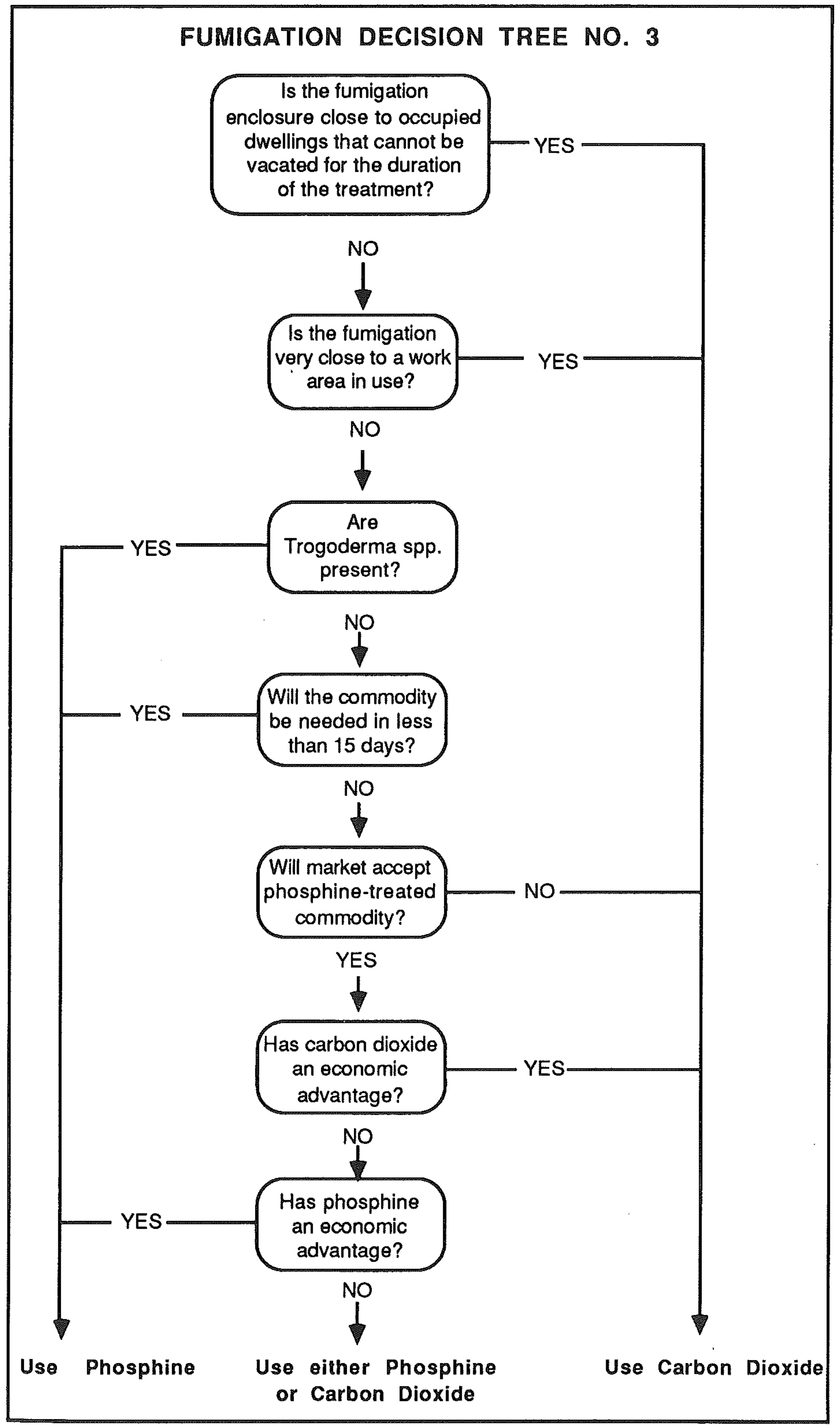
Fumigants can affect the commodity; or the nature of the commodity itself may affect the efficiency of a fumigant. Methyl bromide and phosphine may reduce seed viability, and methyl bromide can taint some products. Sorption of methyl bromide in oilseeds and other high oil content materials can reduce or even stop penetration of this gas into a bulk. A similar problem exists where hydrogen cyanide is used to fumigate high moisture content grains and other products.

Where economic advantage can be gained by marketing a product considered as residue-free the choice of fumigant will be limited to carbon dioxide or phosphine. Carbon dioxide is the only fumigant that is accepted by the bio-dynamic and organic markets, as phosphine fumigation is considered to be a chemical treatment while application of carbon dioxide is not.

The following three 'decision-trees' provide a pathway that allows managers to make the choice of fumigant.







B.2.3. Personnel

A basic requirement is that sufficient personnel trained in fumigation practices are available to carry out all necessary operations in a reasonable time. The fumigator-in-charge should be experienced in fumigation practice and all fumigators should possess a current certificate of competency as fumigators or have an equivalent qualification. Persons without experience should be trained in advance of operations and should work only as fumigators' assistants.

The fumigator-in-charge should be responsible for safe and effective conduct of the fumigation. He should organise and supervise the work of the other fumigators and must be present at all significant stages of the work. He should also undertake:

- the planning of the fumigation and the procurement of materials and equipment;
- the thorough instruction of subordinates with respect to safety precautions, the maintenance and correct use of protective equipment, the general work plan, and the individual tasks;
- the performance of tests for the fumigant gas and the issue of clearance certificates; and
- supervision of the recovery and safe disposal of contaminated fumigation materials.

B.2.4. Materials and Equipment

Adequate supplies of the appropriate fumigant or fumigant-generating materials should be available before commencement of the fumigation. The formulations used should be clearly labelled and give full instructions and warning notices in the local language(s).

Equipment should include: personal safety equipment such as gloves, respirators and respirator canisters, and fumigant detection apparatus; and appropriate fumigant release apparatus such as scales, heat exchanger, distribution lines, nozzles, tablet dispensing apparatus, and flash proof circulation fans. A high level of supervision is required to ensure that this equipment is kept in good working order.

Unless the storage is already suitably sealed for fumigation, there may be a requirement for fumigation sheeting and sealing materials. Wherever possible, all enclosures to be fumigated should be assessed for gastightness before fumigation. Standards of sealing required are described in the other parts of these recommendations giving operational procedures for specific applications, which also cover methods of sealing. Efforts to seal enclosures should be continued until the appropriate standard is met.

Equipment should be available to monitor fumigant concentrations throughout the fumigation. If the storages to be fumigated are far apart, transport for personnel, materials, and equipment will be needed. Walkie-talkie radios may be required for on-site communications.

Large storages also require provision for recirculation of the fumigant. Provision must always be made for venting residual fumigant after treatment.

Secure storage areas must be available for storage of fumigant and fumigation equipment. They should be at least 25 m (27 yards) from dwellings or occupied premises.

B.3. Integrated Commodity Management and Alternatives to Fumigation

To be fully effective, both in terms of benefit cost ratios and in meeting an acceptable level of pest control, fumigation operations, clearly, must be integrated into overall storage operations. Because fumigation disinfests but does not confer residual protection, reinfestation may commence as soon as a fumigation enclosure is opened. Every action must be taken to prevent this and to enhance the effectiveness of fumigation.

B.3.1. Adjuncts to Fumigation

B.3.1.1. Store Hygiene

The basic requirement for good store hygiene is essential to the success of any pest control operation. Store hygiene includes:

- daily sweeping of storages to remove spillage which must be either fumigated immediately or disposed of, preferably by burning (*not* retained within the store);
- regularly cleaning the structure of the storage;
- regularly spraying the fabric of the storage with residual insecticides following cleaning;
- routine inspection of all stocks;
- routine disinfestation of all incoming stocks;
- segregation of all infested stocks; and
- simultaneous fumigation of all stocks within a storage to prevent cross infestation.

B.3.1.2. Gas-Proof Surface

Where commodities are stored in bag-stacks these should be built on a gas-proof surface. This can be done by the use of a gastight plastic floor sheet or specially sealed flooring.

B.3.1.3. Access

Provision must be made for adequate access to bag-stacks so fumigation can be undertaken. A minimum requirement is a space of 1 metre away from walls, other stacks and below any structure supporting the roof of the storage.

B.3.1.4. Use of Internal Liners in Bags

The use of sealable internal polythene liners in bags provides a means of fumigating bagged commodities on an individual basis with phosphine.

B.3.1.5. Stock Management

Stock rotation and control: the principle of first in–first out is a very effective way of avoiding an unacceptable increase in pest numbers.

B.3.1.6. Barrier Sprays

The use of barrier sprays of residual insecticides applied to bag-stacks *before fumigation* provides some measure of protection against reinfestation. Similarly, timed emission of space sprays can be used to delay reinfestation. These are most successful if they coincide with insects peak flight activity, at dusk and dawn. The efficacy of such space sprays is increased in storages where ventilation can be controlled.

B.3.1.7. Pre-heating

Pre-heating a commodity before fumigation can greatly speed up the fumigation process. For example, raising the temperature from 28° to 35°C will break diapause (arrested development) in all diapausing larvae of *Trogoderma granarium* rendering them much more sensitive to fumigant. This would permit a halving of the exposure period or considerably reduction in the fumigant dosage required to control this pest.

B.3.1.8. Cooling after Fumigation

Cooling grain after fumigation will reduce the build up of new insect infestations by providing an unfavourable environment for their rapid growth and development.

B.3.1.9. Sealed Storage

Grain may be fumigated in a sealed storage. A well sealed enclosure will protect commodities from reinfestation for many months without any other treatment.

B.3.2. Alternatives to Fumigation

B.3.2.1. On Site Treatments

Sealing—whether of entire storages or individual bag-stacks—provides a gastight enclosure in which effective disinfestation can be carried out using a controlled atmosphere. This can be created using nitrogen or may be generated, for example, by the controlled combustion of liquid petroleum gas or liquid natural gas. The sealed structure thereafter forms a physical barrier that prevents reinfestation.

Hermetic (airtight) storage effectively controls insects in stored grain and at the same time provides an effective barrier against reinfestation. The penalty inherent in this

method of storage is that some damage must occur to the commodity before the insect infestation kills itself. However, this penalty can be greatly reduced, in large bulks, by the use of very small doses of fumigant. Hermetic storage is as applicable on a large scale, for example Cyprus bins (1500 tonne capacity), as it is on a small scale, for example Wise Joseph Sacks, with a capacity of up to 50 kg.

Admixed grain protectant insecticides will protect commodities for a time which depends on the applied concentration. They are most effective when applied to uninfested grains as they are taken into storage. Residual insecticides, however, are largely ineffective when applied to heavily infested grain. Application of residual pesticides as a barrier to the outer surface of bag-stacks is ineffective and will lead to selection of resistant strains of insects.

The use of automatic emissions of contact insecticides to control flying insects in storages maintained at a high level of hygiene can be useful.

Grain may be cooled and stored at temperatures at which insect growth and development are reduced or halted. This can be achieved by refrigerated aeration and is particularly useful when grain has to be stored at a high moisture content.

Trapping as a direct control measure can only have a palliative and cosmetic effect, except in storages maintained at a very high level of hygiene.

B.3.2.2. Alternatives that Involve Moving the Grain.

Infested grain may be offered for immediate sale thereby removing the problem from the storage. In some cases in-transit fumigation may be possible, for example in barges, lighters, shipping containers, and bulk grain carriers.

Some grains can be disinfested by processing, for example paddy, which is milled and polished before consumption.

In cases where an infestation is not considered too serious or extensive, it may be diluted by blending it with uninfested grain.

Heavily infested grain may be down-graded and offered for sale as animal feed, or compounded into animal feed.

Infested grain may be 'cleaned' by a physical separation process, for example running the grain over an inclined screen, or aspirating it to remove external insect infestation, but this will not control internal insect infestations.

Protectant insecticides may be admixed to the infested grain. However, residual insecticides are largely ineffective when applied to heavily infested grain. This procedure does not lend itself to bagged grains where the cost of treatment will also involve bulking and rebagging the grain. It may prove to be more economical to dispose of the grain at a discount.

Infested grain may be disinfested by controlled heating. This is most effectively achieved by fluidising the grain in hot air. The process also allows the grain to be cleaned, an obvious advantage where removal of filth may be an important consideration.

Wet grain, which is particularly susceptible to insect (and mould) damage, may be dried and thereafter treated with grain protectant insecticides for prolonged storage safety.

Where permitted, irradiation with gamma rays may be an option. However, this process leaves living, though sterilised, insects in the grain after treatment, which may be unacceptable when the grain is marketed.

B.4. Investigation of Failures

The assessment of whether a treatment succeeded and investigation of failures should be an integral part of fumigation management. Remedial action can then be planned to avoid new and further failures, and optimise procedures.

Fumigation must be deemed to have failed if measurements of fumigant concentration throughout the fumigation interval do not confirm that an adequate concentration × time (Ct) product has been attained, even though no live insects are found immediately after fumigation.

In cases where a natural infestation was evident at the time of treatment, some evidence of the efficacy of the fumigant may be obtained by inspecting the treated commodity following the fumigation and ventilation. Visual inspection of insects from half kilo grain samples, taken according to standard sampling procedure, will be required.

Such inspection will give an estimate of the mortality of adult stages, but detection of any surviving immature stages generally requires incubation of grain samples. These should be held in ventilated containers at 25–35°C for six weeks before being re-examined. Both phosphine and carbon dioxide are substantially more active against adult insects than their immature stages. All adults may be killed, yet many immatures survive. Incubation of samples or continued monitoring of the commodity bulk thus forms an important part of the assessment of a treatment with these materials.

It is important that fumigation failures are drawn to the attention of management, so that the causes of failure can be determined and appropriate action taken to avoid them in future.

SECTION C. General Fumigation Procedures

Fumigant application is a complex operation that needs careful planning, an understanding of the process by those involved, and stringent precautions to ensure that it is carried out safely. Because compounds highly dangerous to man are involved, many countries have enacted legislation to control fumigant use so only trained and licensed personnel are permitted to supervise fumigations and apply the materials commercially. Small scale agricultural use is sometimes exempt from restrictions, but strict safety precautions must still be taken during fumigant use under such conditions.

Because of the hazardous nature of the fumigation process, it is useful to carry out treatments according to a recognised code of practice that is accepted by all parties involved. Indeed, in many situations, following the local code of practice will be mandatory. Where a locally recognised code is not available, certain general texts are available describing the detail of fumigation, but these are a poor substitute for a set of recommendations designed for specific application in defined areas. This set of recommendations aims to provide for the ASEAN region details of the standards that should be imposed on fumigators for the conduct of their operation. This section describes general fumigation procedures, including those features concerned with efficacy and safety. The principles inherent in any fumigation are outlined without defining specific fumigations. The following section considers each fumigant separately and describes in principle the standards associated with the conduct of a fumigation with a particular material, including detailed dosage recommendations. **Sections C and D** together comprise a description of general fumigation procedures and codes of practice for use of particular fumigants in a format and with technical detail appropriate for inclusion in any regulations formulated nationally to guide the industry along paths of sound fumigation practice.

C.1. Scope and Application of Recommendations

The recommendations proposed have been aimed primarily at fumigation of grain and related commodities in some form of central storage. Fumigation in farm stores follows the same principles and general procedures but differs in some operational procedures. The recommendations provide for the minimum standards that must be achieved if fumigations are to be successful and reliable. *If the standards cannot be achieved fumigation should not be attempted and control of pests should be sought by other means.*

The standards have been based on a level of sealing and construction of the enclosure, whether it be a permanent structure or a sheeted stack, that will allow pressure testing for gastightness. It is recognised that the technology of pressure testing may not be immediately applicable, and an interim compromise is embodied in the recommendations, relying on good construction of the fumigation enclosures and monitoring of gas concentrations during fumigation. The eventual goal is that all enclosures be tested to determine their gastightness before fumigation.

C.2. Safety Considerations

The basic safety principle in the conduct of fumigations is that personnel should not be required to enter any area containing any significant content of the fumigation material. All operations should be designed to meet this requirement and appropriate modifications made to fumigation equipment and enclosures. This particularly concerns application of the fumigant and subsequent opening of the enclosure for airing. These are the operations during which the greatest risk occurs of accidental exposure to harmful concentrations of fumigant. Because of the risk of accidental exposure, protective equipment must be worn as appropriate and be available for rescue purposes.

C.2.1. Monitoring Health of Operators

It is essential that the employer institute a compulsory program of monitoring of the health of fumigation operators. Advance warning of the development of medical conditions incompatible with work as fumigation operators will enable measures to be taken to lessen the risk of occupational health problems developing in the operators. Moreover, it may also help prevent medical conditions being wrongly attributed to the effect of the fumigants.

C.2.2. Fumigation Personnel

C.2.2.1. Minimum Number of Persons

There should never be fewer than two people present during the introduction and removal of a fumigant, irrespective of how small the dosage or how restricted the extent of the fumigation. One of these people should always be designated as the fumigator-in-charge and be appropriately qualified (see next section). In emergencies, where a person becomes incapacitated in a fumigation enclosure or risk area, the rescue team must include *one person who does not enter* the enclosure or risk area. It is this person's sole duty to seek further assistance in the event of the rescuers also succumbing.

C.2.2.2. Qualifications of Personnel

At least one member of the work force employed in each fumigation should be a trained and experienced fumigator, holding (where applicable) a fumigation licence issued by the appropriate health department or registration authority. He should be designated fumigator-in-charge and be given responsibility for the safe and effective execution of the work. He must be present at all times during the active phases of each fumigation. In addition to the organisation and supervision of the work of his subordinates, his duties should include:

- the planning of the fumigation and the procurement of materials and equipment;
- the thorough instruction of his subordinates with respect to safety precautions, the maintenance and correct use of protective equipment, the general work plan, and individual tasks;

- pressure testing;
- the performance of tests for the fumigant gas during and after the fumigation, and the issuing of clearance certificates; and
- supervision of the collection and safe disposal of empty cylinders and any other contaminated empty packaging materials.

C.2.3. Safety Equipment

The fumigator in charge must be responsible for the care and general maintenance of all safety equipment.

C.2.3.1. Breathing Apparatus

Two basic types of apparatus are available. Positive pressure breathing apparatus is used when there is possibility of exposure to significant air contents of fumigant or to atmospheres deficient in oxygen. Full-face canister respirators are used as insurance protection against accidental exposure to the fumigant.

The breathing apparatus should be self-contained, using portable air tanks charged by oil-free compressor. Each operator using this type of breathing apparatus must work in association with another operator who is outside the area where there is risk of exposure. *All rescue operations should involve use of this type of apparatus.*

Full face canister type respirators are the most commonly used devices for protection against accidental exposure to fumigants. Each operator should be supplied with a personal respirator and be responsible for its day-to-day maintenance. The face piece must fit the operator correctly. This can be tested by closing the inlet to the container with the ball of the hand and inhaling deeply so that the low pressure created will cause the face piece to collapse against the face for at least 15 seconds. Specific canisters are required for use with each fumigant and the types are not interchangeable. Canisters may be fastened directly to the face piece or carried on the back of the operator and connected by flexible hose to the face piece. Canisters should be resealed with the original top and bottom seals between uses.

Breathing apparatus should be stored in a cool, dry place away from any exposure to fumigants. Records must be kept of every use. With canisters, the dates of manufacture and expiry must also be recorded, together with the dates on which the top and bottom seals are removed. Canisters that are not used within 6 months of breaking of the bottom seal over the inlet valve must be discarded even if there is no exposure to fumigant. Canisters must also be discarded after prolonged exposure to low concentrations of fumigant or any accidental exposure to high concentrations. In practice, the canister will be discarded after any fumigation in which there is exposure to fumigant and in prolonged usage during a fumigation it should be discarded after 1 hour of wearing if any low-level exposure has occurred. This period can be extended to, at most, 2 hours if fumigant concentration is minimal.

Damaged canisters must not be used, as any rearrangement of the contents may affect efficient removal of fumigant from the atmosphere. All discarded canisters should have the inlet port damaged to prevent accidental reuse. With canisters generally, if there are any doubts, discard them.

C.2.3.2. Protective Clothing

As well as appropriate breathing apparatus, operators releasing all fumigants except carbon dioxide should wear completely buttoned boiler suits (coveralls or overalls) and protective gloves and footwear.

C.2.3.3. Safety Harness and Ropes

When fumigators are required to enter fumigation enclosures that are difficult to access, safety harnesses and lifelines must be worn.

C.2.3.4. Detection Equipment

Appropriate detection equipment, e.g. halide lamps, conductivity meters, and detector tubes, should be on hand for the fumigants proposed for use. The equipment should be tested regularly and maintained in good working order at all times.

C.2.3.5. Lighting

Adequate lighting, including approved design torches, should be available for all fumigations. The lighting equipment should be suitable for use in flammable atmospheres, including those generated from grain dust.

C.2.4. First Aid Provisions

C.2.4.1. Instruction in First Aid

All fumigators and their assisting personnel should be instructed in first aid and other emergency procedures specific to fumigation.

C.2.4.2. Medical Kit

A first aid kit including items specific to fumigation should be available at all times. Advice on the content of this kit should be sought from the appropriate government health authorities.

C.2.4.3. Recovery of Affected Personnel

Protective clothing and self-contained breathing apparatus must be used when recovering affected personnel from areas where fumigants are present. The affected personnel should be moved to fresh air, placed in a restful position and kept warm while awaiting medical attention.

C.2.4.4. First Aid Treatment

When an accident occurs, first aid treatment must be started at once. If possible, one person should begin treatment while another calls a doctor and ambulance, giving details of fumigant and circumstances of exposure.

Where practicable, the following measures shall be carried out while awaiting the arrival of medical aid:

- apply artificial resuscitation and external cardiac massage, if required
- loosen all tight clothing
- remove contaminated clothing, including shoes, socks, wrist watch, and spectacles
- thoroughly wash contaminated skin with clean water
- eye contamination
  - hold eyelids open and wash eyes immediately with a gentle flow of water
  - continue washing until doctor arrives
  - do not use any chemicals, as they may increase the injury.

C.3. Action Before Fumigation

C.3.1. Notification of Authorities and Persons Concerned

C.3.1.1. Fumigation of a Building or Enclosed Space

A fumigator intending to treat a building or other enclosed space outside the premises of an approved fumigation company shall deliver an appropriate notice in writing (see Appendix 2) 24 hours before the fumigation commences, to:

- the nearest Police Station and Fire Brigade
- every tenant or occupier within the fumigation enclosure and risk area, who must acknowledge receipt by signing the duplicate copy which shall be retained by the fumigator
- the authority concerned with plant quarantine matters
- the division of the Health Department that deals with occupational health matters
- other health authorities as appropriate.

C.3.1.2. Fumigation of a Ship

The fumigator in charge, when intending to fumigate a ship or other vessel, shall deliver a notice in writing in the form of Appendix 2, before the fumigation commences to:

- the appropriate Port Authority;

- the appropriate Police Station and Fire Brigade; and

- the master or other person in charge of the vessel, who must acknowledge receipt by signing the duplicate copy which shall be retained by the fumigator.

C.3.2. Fumigation Warning Signs

The fumigator in charge of fumigation of any building, vessel, or enclosed space shall, before the application of the fumigant, affix to each door and other means of access to the fumigation enclosure, a notice in the form of Appendix 3 with a white background on which there shall be printed, in the local language(s), the message **'DANGER KEEP OUT'**, followed by the words **'FUMIGATION WITH [Name of Fumigant]'** in capital letters not less than 10 cm (3 inches) high, in a contrasting colour to the background.

The fumigator's name and telephone number should be clearly shown at the foot of the notice. All warning notices should be suitably illuminated at night.

C.3.3. Precautions and Tests of Equipment

No person shall commence a fumigation until the following conditions apply:

- The fumigator has by personal inspection ascertained that all portions of the fumigation enclosure and risk area have been vacated.

- All fires and naked lights within the fumigation enclosure have been put out. For flammable fumigants, there should be no smoking or carrying of matches and cigarette lighters inside the risk area.

- All liquids and foods that are not required to be included in the fumigation and might be affected by the fumigant are removed from the fumigation enclosure.

- All cracks, crevices, or openings in or between walls and ceilings or roof and floors and all fireplaces in the building, vessel, or other enclosed space about to be fumigated have been sealed to prevent the escape of fumigant from the fumigation enclosure.

- Fans as required are in position and tested for efficiency. For flammable fumigants, it is essential that fans and their switches, if any, used within the fumigation enclosure comply with the requirements of hazardous locations and are flash proof.

- The nearest operable telephone outside the fumigation area has been located and its number noted.

C.3.4. Testing for Gastightness

Wherever possible, all enclosures to be fumigated should be assessed for gastightness before fumigation. Standards of sealing required are described in the

separate parts of these recommendations giving operational procedures for specific applications, which also cover methods of sealing. If necessary, enclosures should be further sealed until the appropriate standard is met.

The three types of test available for determining the sealing level of an enclosure are described in Appendix 5.

C.4. Fumigation Procedure

C.4.1. Fumigation Process

The efficacy of all fumigants is dependent upon a suitable concentration and duration of fumigation. The instructions for the particular fumigant, volume of the space being fumigated, goods to be fumigated, and pest to be controlled should be followed. (For specific guidance on sources of information, refer to **Section D** and to the separate parts giving operational procedures for specific applications). The instructions should be consulted beforehand and followed in detail. Under no circumstance shall the fumigant concentration be grossly different from the recommended concentration, which is based upon scientific experiment.

C.4.2. Ventilation

Provision for ventilation should be made during the preparation of structures for fumigation. Where possible, two openings to facilitate flow-through ventilation should be fitted to the structure, with temporary seals that can be removed from the outside of the fumigation enclosure at the end of fumigation. Doors, windows, or hatches selected for this purpose should be arranged so that they may be opened from the outside of the fumigation enclosure. Where fans are used, these may be operated intermittently to allow for desorption of fumigant from commodities. Where fans are run continuously, no reduction in the nominal ventilation period should be made.

C.4.3. Introduction of Fumigant

Fumigants should be introduced to the fumigation enclosure in accordance with specific fumigation instructions and safety measures, taking care to ensure that all application equipment is gastight and that the correct dosage is applied.

Liquid fumigants should be introduced from outside the fumigation enclosure. The enclosure should be vacated by all personnel before the fumigant is released. The fumigant must be applied in such a way that it does not come in contact with goods or structures while in liquid form.

Solid fumigants may be introduced while within the enclosure. This should be undertaken as a carefully planned and rehearsed operation by the fumigator-in-charge after all other personnel have left the enclosure.

Whenever it is necessary to wear a safety harness, at least one other member of the fumigation staff shall remain in the immediate vicinity and in clear sight of the operator. Adequate provision shall be made to haul out the operator (e.g. with a lifeline) in an emergency.

C.4.4. Watchman

Where the fumigation enclosure and risk area cannot be satisfactorily secured by locking, a watchman shall be on duty. Even with a locked premises, it is recommended that a watchman be present during the exposure period. The watchman must remain well outside the established risk area.

C.4.5. Detection of Leaks

During and after the introduction of the fumigant, the fumigator-in-charge, wearing a respirator, shall inspect both visually and with appropriate detection apparatus, for leaks in equipment and in the fumigation enclosure. The following action should be taken if leaks are detected:

- Seal and re-test any leaks located, to ensure that the fumigation enclosure is gastight.

- In the event of a massive accidental release of fumigant, evacuate the risk area immediately and inform appropriate emergency and disaster agencies.

C.4.6. Removal of Fumigant

At the end of the required fumigation period, the fumigant should be removed by controlled release into the atmosphere, ensuring that:

- the risk area is free from all unauthorised persons;
- the fumigation team is properly equipped, in accordance with **Section C.2**; and
- ventilation of the fumigation enclosure is done by mechanical means, where available. Where mechanical ventilation is not available, the enclosure should be unsealed in sections, to allow gradual release of the fumigant. Where natural ventilation is insufficient for rapid clearance of the gas, fans may be used.

C.4.7. Checking for Clearance

The risk area shall be checked for clearance of the fumigant as follows:

- After a sufficient period of ventilation, the fumigation team, equipped as described in **Section C.2**, should check the concentration of fumigant in the risk area and, if it is acceptably low, should proceed to check the fumigation enclosure.

- If an excessively high concentration of fumigant is detected, the fumigation team must retire, wait a further period of time and recommence the check procedure until all sections of the fumigation enclosure have been proved safe for re-entry.

C.5. Action After Fumigation

C.5.1. Re-entry into the Fumigation Area

When fumigant concentrations in the fumigation enclosure and risk area have fallen to a safe working level, operators may re-enter the areas to remove fumigation equipment.

C.5.2. Clearance Declaration

When fumigant has been successfully removed, a formal clearance declaration shall be issued. An appropriate form is given as Appendix 4.

C.5.3. Fumigation Records

Every person in charge of a fumigation shall keep a record of the fumigation. The record shall include the following details:

- address of fumigation enclosure

- fumigant used*

- time fumigation commenced*

- time fumigant cleared*

- any fumigant concentration recorded, in association with assessment of effectiveness specified below*

- copies of all notices submitted

- an assessment of the effectiveness of the fumigation (details of the conduct of this will be provided later, in the descriptions of operational procedures for specific applications).

Items marked with an asterisk should also be recorded on stack/bin cards.

SECTION D.
Codes of Practice for Fumigation

D.1. Phosphine

The following code is designed to establish the principles for effective fumigation with phosphine. These principles cover both safety and efficacy. Operational procedures incorporating them, applicable to specific types of fumigations, are given in the other parts of the recommendations relating to use of phosphine.

Phosphine has come into prominence as an effective fumigant to control insects in grain and a number of other stored products. This is largely the result of the development of methods whereby the gas can be generated within a grain mass without undue risk of either fire or excessive exposure of fumigators. Safe and effective fumigations with phosphine will result only if fumigators adopt sound working procedures.

Preparations for generating phosphine should not be applied to grain in transit unless an appropriate standard of gastightness is achieved for the vessel or container and suitable means of venting the fumigant are available. Methods of sealing and gastightness testing are given in Appendix 5 and, in more detail, in the separate parts describing operational procedures for specific applications.

D.1.1. Objectives and General Requirements

The tolerance of the developmental stages of insects to phosphine varies considerably. Eggs and particularly pupae are much more tolerant of phosphine than larvae or adults. Although control strategies for most fumigants are based on the application of a dosage that is high enough to kill the most tolerant stage, this is normally not the case with phosphine. In most cases a dosage is applied that is sufficient to kill larvae and adults only. *The key to effective fumigation with phosphine therefore depends on holding the gas long enough for the more tolerant eggs and pupae to continue their development to larvae and adults, whereupon they succumb.*

Clearly, it is essential to retain the gas for long enough for this development to occur. This may be achieved by fumigating only in gastight enclosures or using a method of application in near gastight enclosures that provides a continuous input of phosphine. Fumigations in which most gas is lost by about the fifth day, or even just from pockets within the enclosure, will fail, and yet—in killing the mobile and thus more visible larvae and adults—will create an illusion of success.

When and when not to use phosphine as a fumigant

Phosphine is the fumigant of choice:

- when a commodity is required in not less than 7 days
- when *Trogoderma granarium* is present and use of methyl bromide is not mandatory
- when oilseeds*, expeller cake, and meals must be treated
- where germination is important
- where commodities have been treated previously with methyl bromide
- where taint may be a problem if methyl bromide is used, e.g. on flour

Phosphine should not be used:

- where resistance is known to exist in an insect population
- in unsealed enclosures
- at temperatures below 15°C
- where a rapid treatment is required, i.e. less than 7 days
- in areas immediately adjacent to workspaces and habitations
- where there is no trained, qualified, and properly protected fumigation team.

*Residue data not yet available.

D.1.2. Phosphine as a Fumigant

D.1.2.1. General Characteristics and Warning Properties

Phosphine is only slightly heavier than air and disperses more rapidly than other fumigants. It is not strongly sorbed by commodities and has great penetrative capacity. The standards of gastightness required for effective fumigation with phosphine are at least as high as those required for other fumigants (e.g. methyl bromide).

The basic properties of phosphine are as follows:

formula	PH_3
molecular weight	34
boiling point (°C)	–87
specific gravity (gas) [air = 1.0]	1.2
vapour pressure at 30°C (atm)	42
conversion factor, g/m^3 to ppm (30°C, 1 atm)	730
flammability limits in air (v/v)	>1.7%
solubility in water (v/v)	0.2

Pure phosphine is colourless and odourless. In practice, however, impurities in the gas produced possess a characteristic odour that in most instances makes phosphine detectable at concentrations down to less than the hygienic standard of 0.3 ppm (parts per million = mg/kg). The odour associated with phosphine is described as resembling garlic or calcium carbide, or impure acetylene. Absence of odour *does not,* however, necessarily indicate absence of phosphine, as the odorous impurities can be removed easily by adsorption, for example on flour, leaving phosphine without a smell.

Phosphine is only slightly soluble in water and has low solubility in most solvents. It reacts with copper and copper-containing alloys such as brass, and with precious metals. This reaction results in corrosion of the metals, which is manifested by a darkening of surfaces, accompanied by the formation of acids. The reaction is enhanced in the presence of ammonia, which is given off during the decomposition of some proprietary formulations. The reaction is further enhanced by moisture and in air containing salt, as found near the sea.

As a result of its reaction with copper, phosphine may damage electrical equipment such as meters, wiring, switches, fire alarm systems, and electronic systems. Where copper components are not well sealed, steps should be taken to seal or cover such components before fumigation with phosphine. A coating of grease or vaseline provides protection in many situations.

Phosphine is reported to be spontaneously flammable at temperatures above 100°C and at reduced pressures, especially in dry atmospheres. Concentrations of phosphine above 1.7% in air form an explosive mixture. However, commercial preparations that produce phosphine either contain substances that reputedly reduce the fire hazard or substances that control the rate of production of phosphine from the phosphide, thus restricting the concentration of phosphine generated close to the formulation.

D.1.2.2. Adverse Effects on People

Since phosphine is highly toxic, exposure of humans to even small amounts should be avoided. Poisoning can result from inhalation of the gas or ingestion of tablets or pellets of the formulation, but the gas is not absorbed through the skin. Inhalation of phosphine may produce symptoms including nausea, vomiting, diarrhoea, headache, and chest pain which can precede death due to massive accumulation of fluid in the lungs (pulmonary oedema). Very brief exposures to a concentration of 2.8 mg/L (*c.* 2000 ppm in air) are lethal to humans. The hygienic standard is usually set at an average concentration of 0.3 ppm for a normal 8-hour working day and 40-hour working week. Although the use of average concentrations permits excursions above this limit, in operational terms the aim should be to treat it as the maximum acceptable level.

D.1.2.3. Adverse Effects on Commodities

Phosphine is only slightly absorbed by most foodstuffs and most of it is easily removed by subsequent ventilation. Any phosphine reacting with the commodity is reported to produce harmless residues. At normal dosages, phosphine appears to

have virtually no effect on the germination of seeds held at safe moisture contents, but it may slightly reduce the vigour of subsequent seedlings. There is some evidence that phosphine may reduce germinability if applied to high moisture grain.

D.1.2.4. Detection and Measurement

The most convenient direct-reading method for the detection and determination of phosphine in air involves the use of detector tubes containing a material that stains when air containing phosphine is drawn through it. Since commercially available tubes vary in sensitivity and accuracy, the advice of occupational health authorities should be sought before detector tubes and pumps are purchased. Whichever brand of tube is used, the manufacturers' directions should be followed exactly.

Other methods, including stains on paper discs or tape, or portable electronic devices should be used with caution. Photo-ionisation devices, for example, are also sensitive to a wide range of other gaseous substances that could be present in the fumigation area.

Suitable detection equipment must be available for use at all fumigations, and persons involved in the fumigation must be competent in using the equipment and interpreting the readings obtained.

D.1.3. Personal Protection

D.1.3.1. Respiratory Protection

Fumigators and other persons at risk from inhaling excessive quantities of phosphine must be provided with either a full-face canister respirator or an open-circuit, self-contained breathing apparatus with full face mask. Respiratory protection must be worn whenever tests of the atmosphere reveal concentrations of the gas greater than the hygienic standard (currently 0.3 ppm v/v in most countries).

Masks and canisters should be issued on a personal basis and a register of use maintained by the fumigator-in-charge.

D.1.3.1.1. Canister Respirators

Canister respirators should be fitted with a canister designed for protection against phosphine, as recommended by occupational health authorities. Each time a respirator of this type is put on for use, the facial fit should be tested by closing the inlet to the canister with the palm of the hand and inhaling deeply; the vacuum so created should cause the facepiece to adhere to the face for about 15 seconds. With this type of respirator it is essential that the canister be used within its stated shelf life.

The respirator canister must always be replaced before either its shelf life has expired or the recommended usage time has been reached. The expiry date of a canister may easily be calculated since each is marked with the date of manufacture and shelf life.

Canisters should be stored in a cool, dry, well-ventilated place away from contamination by any fumigants. The following precautions should always be observed:

- When the canister is attached to the respirator facepiece after the top seal is removed, record the date. This is best done by writing the date on a small adhesive label which must be affixed to the canister. This label can be used as a 'log' to record exposure of the canister to the fumigant.

- Before using the respirator, remove the cap and the seal over the air inlet valve of the canister. Again, at this time mark the date on the 'log' label. Once this seal is removed, even if there is no exposure to fumigant, dispose of the canister after a lapse of 6 months.

- After any fumigation in which there has been prolonged exposure to low concentrations of the fumigant or accidental exposure to high concentrations, immediately discard the canister. As a guide, 1 hour of wearing is the usual period after which a canister should be discarded. This could be extended to 2 hours, but only when exposure is minimal. *Allow a wide margin of safety in estimating exposure times, as canisters cost little in terms of health of the individual.* If there is any doubt about the exposure life of the canister, discard it.

- Canisters should be resealed with the original top and bottom seals between uses.

- When canisters are discarded, they should be rendered unusable by mutilating the inlet port and disposed of under conditions which will prevent them from being picked up and used again.

- Canisters that show any sign of external damage must be considered worthless, and should be discarded. A severe blow on the metal covering may cause displacement of the contents, permitting contaminated air to pass through to the wearer.

- Immersion of the canister in water makes it useless. Water may enter the canister through the facepiece. Disconnect the hose and canister when cleaning or disinfecting the facepiece.

D.1.3.1.2. Self-contained Breathing Apparatus

Self-contained breathing apparatus is to be preferred wherever this equipment is available. The facial fit of this type of apparatus may be tested in a manner similar to that employed with the canister respirator, except that the cylinder valve is closed prior to deep inhalation.

D.1.3.2. Skin Protection

Gloves should always be worn when phosphine-generating tablets, pellets, or sachets are handled. Disposable plastic gloves are satisfactory.

D.1.4. Fumigation Personnel

D.1.4.1. Minimum Number of Persons

At least two people should always be present during the introduction and removal of fumigant, irrespective of how small the dosage or how restricted the extent of the fumigation. One of these people should always be designated as the fumigator-in-charge (see next section).

D.1.4.2. Qualifications of Personnel

At least one member of the work force employed in each fumigation should be a trained and experienced fumigator, holding (where applicable) a fumigation licence issued by the appropriate health department or registration authority. He should be designated fumigator-in-charge and be given responsibility for the safe and effective execution of the work. He must be present at all times during the active phases of each fumigation. In addition to the organisation and supervision of the work of his subordinates, his duties should include:

- the planning of the fumigation and the procurement of materials and equipment;

- the thorough instruction of his subordinates with respect to safety precautions, the maintenance and correct use of protective equipment, the general work plan, and individual tasks;

- the performance of tests for the fumigant gas and the issuing of clearance certificates; and

- supervision of the collection and safe disposal of potentially contaminated packaging materials.

D.1.4.3. Monitoring of Health of Fumigation Staff

Where staff are part of a regular fumigation team, *the fumigator-in-charge should ensure that regular health checks are performed on himself and his staff.* This should be done in consultation with, and according to the requirements of, local health authorities.

D.1.5. Fumigation Practice

D.1.5.1. Formulations

D.1.5.1.1. Metal Phosphides

Phosphine may be obtained from the hydrolysis (reaction with water) of a range of metal phosphide formulations. Aluminium phosphide preparations are most common but magnesium phosphide-based materials are also available. Calcium and zinc phosphides have been used as phosphide sources, but are not recommended for direct use with grain.

The following types of formulation are in use:

- Tablets and pellets: these are available in a variety of containers some of which may be resealed when less than the contents of the container are required. Others are not resealable and once opened the entire contents should be used immediately.

- Sachets and bags containing powder: these are packaged in strings that tie the sachets together, as individual strengthened bags with eyelets to facilitate probing into grain, or as 'blankets' containing rows of sachets in a fabric strip.

- 'Plates' in which the metal phosphide formulation is sealed and packed in metal foil contained in a plastic matrix. These may be packed individually in sealed metal foil bags or in strips of several plates joined together and sealed in a tin.

Under tropical conditions, aluminium phosphide preparations are to be preferred over those of magnesium phosphide. The more rapid release of phosphine claimed for the latter confers no advantage, while the higher reactivity to liquid water may give rise to safety hazards.

D.1.5.1.2. Cylinders of Compressed Gas

In addition to metal phosphide formulations, phosphine is available as a gas from cylinders in which it is mixed with a carrier or diluent such as carbon dioxide.

D.1.5.2. Storage and Handling of Formulations

D.1.5.2.1. Metal Phosphides

Stocks of any preparation which contains metal phosphide must be stored under lock and key in dry, well-ventilated premises. Warning notices specifying the danger of unauthorised entry should be placed in prominent positions at all points of access to the store. All formulations should be handled with care. *Spontaneous combustion may occur when sealed packages containing metal phosphide preparations are opened, and containers should not be opened in an atmosphere where there is a risk of dust explosion.*

If unable to use the whole contents of tubes containing tablets of phosphide at once, replace the lid of the tin and seal it with flexible PVC tape (e.g. electrical insulating tape). This permits storage for, *at most,* a week. Flasks with screw caps, on the other hand, may be stored for one or two months after opening, provided the stopper is firmly replaced.

Metal phosphide formulations should never be exposed to free water because of the danger of fire or explosion. Also, tablets and pellets should not be placed in closely packed groups for fumigation because heat is released during gas evolution and excessive heating in one location could be a fire hazard.

At the end of a fumigation in which metal phosphides have been used, the powdery residues that remain contain mostly metal hydroxide and a small amount of

undecomposed metal phosphide. Under normal circumstances of grain handling these residues do not present a hazard, but it is nevertheless desirable to remove them if possible.

D.1.5.2.2. Cylinders of Compressed Gas

Cylinders containing phosphine should be stored and handled in accordance with local regulations governing the handling and storage of compressed gases.

D.1.5.3. Preparation for Fumigation

D.1.5.3.1. Planning

Before commencing a treatment, the fumigator-in-charge should prepare a plan describing the intended course of the fumigation. He should explain this plan in detail to persons involved in the fumigation, allocating responsibilities for particular aspects of the plan where appropriate. The plan should include how the fumigant is to be applied, how the enclosure is to be sealed, how the fumigant is to be vented after the treatment, at what times the various actions involved in the fumigation are to be carried out and who will carry them out.

D.1.5.3.2. Notice of Intention to Fumigate

An authorised fumigator intending to fumigate a building or other enclosed space shall deliver a notice in writing 24 hours prior to the fumigation commencing, in the form of Schedule No. 1 (see Appendix 2) to:

- the appropriate authority;

- the nearest Police Station and Fire Brigade; and

- every tenant or occupier within the fumigation and risk area who must acknowledge receipt by signing the duplicate copy which shall be retained by the fumigator.

D.1.5.3.3. Definition of Risk Area

There is a risk area around a fumigation enclosure comprising all adjacent spaces in which harmful concentrations of the fumigant might, in the opinion of the fumigator-in-charge, become present. The risk areas may be entered only by permission of the fumigator-in-charge. It should be conspicuously marked to warn people not involved in the fumigation operation not to enter the area. Warning notices must display the identity of the fumigant and the name and address of the fumigator-in-charge, together with emergency telephone numbers. Special care should be taken over buildings or rooms with walls common to an area that is to be fumigated. Leakage into such spaces can often occur. They are thus normally included in the risk area. Where necessary, the fumigator-in-charge should take possession of any keys to doors in the fumigation and risk areas.

D.1.5.3.4. Testing of Probes or Dispensers

Probes or dispensers which are to be used to add the phosphide formulation to grain should be tested to ensure that they are in good working order. In order to ensure that correct dosage will be achieved, the settings of automatic pellet dispensers used for treating commodities going into bulk storage should be checked in relation to the loading rate of the conveyor system servicing the cell in which the grain is to be treated.

D.1.5.3.5. Sealing of Fumigation Enclosures

When metal phosphide formulations are used as the phosphine source, fumigation enclosures should, in the interests of both safety and effective fumigation, be sealed as thoroughly as possible to minimise leakage.

Bag stacks to be fumigated should be constructed on top of a gas-proof ground sheet or on an impervious floor e.g. a concrete floor painted with a sealing paint. Cover sheets should be undamaged and sealed to the ground sheet.

Silos and other structures such as sheds or godowns that are to be used as the fumigation enclosure should be sealed to the appropriate gastightness standard if phosphine applied as phosphide is to be used effectively. This standard is consistent with a decay of an excess internal pressure from 500 Pascals (Pa), or 2" water gauge, to 250 Pa (1" water gauge) in not less than 5 minutes in filled enclosures.

Some systems of application, using phosphine dispensed from cylinders, may permit effective fumigation of somewhat less well sealed structures. Safety and sealing standards for these methods have not yet been fully established.

Methods of sealing and testing for gastightness are given in Appendix 5 and, in more detail, in the separate parts giving operational procedures for specific applications.

D.1.5.3.6. Provision for Ventilation of Fumigation Enclosures

Provision for ventilation should be made during the preparation of structures for fumigations. With bag stacks this is of less importance because it is usually not difficult to safely remove the sheets. However, with silos or godowns preparation before fumigation may be desirable. Where possible, when silos or godowns are to be fumigated, two openings to facilitate flow-through ventilation should be provided. They should be provided with temporary seals that can be removed from the outside of the fumigation enclosure at the completion of fumigation. Doors, windows, or hatches selected for this purpose should be arranged so that they may be opened from the outside of the fumigation enclosure. Where fans are used, these should comply with the general requirements for fans outlined in **Section** C of these recommendations. Where fans are run continuously, no reduction in the nominal ventilation period should be made.

D.1.5.3.7. Ventilation of Adjacent Areas

Where people may have to work in, or pass through, areas immediately adjacent to a fumigation enclosure, good ventilation of the areas should be provided. The natural ventilation induced by opening doors and windows may have to be supplemented with mechanical ventilation to ensure that the hygienic standard is not exceeded.

D.1.5.3.8. Warning Signs

The fumigator-in-charge of the fumigation of any building, vessel, or enclosed space shall, immediately before the application of fumigant, affix a warning notice to each door and other means of access to the fumigation area. These notices should have a warning symbol appropriate to the country/culture concerned and have printed on them, in the local language(s), the following English text:

DANGER–KEEP OUT
POISON GAS
FUMIGATION WITH PHOSPHINE

The notices should have a white background and the printing should be in capital letters not less than 10 cm (3 inches) high, in a colour that stands out from the background.

The authorised fumigator's name, contact address, and telephone number must be clearly shown at the foot of the notice. The form of notice suggested is shown in Appendix 3.

All warning notices should be suitably illuminated at night.

D.1.5.3.9. Final Safety Checks

Canister respirators should be checked to ensure that the valves in the facepiece are undamaged and functional, and that the correct type of canister is being used. Self-contained breathing apparatus should be checked to ensure that facepieces are functional and that air cylinders have been charged. Phosphine detector tubes should be checked to ensure that they have not exceeded their shelf life; pumps should be free from leakage. A flameproof electric hand torch should be available to facilitate inspections and the reading of detector tubes.

Before finally sealing any fumigation enclosure, especially those with easy worker access, all accessible places within the enclosure must be inspected by the fumigator-in-charge to ensure that all personnel have left the enclosure. Immediately after the inspection, the fumigator in charge will ensure all access points are closed securely and fumigation warning notices are in place.

D.1.5.4. Application of Metal Phosphide Preparations

Respirators need not be worn when tablets or pellets are dispensed under conditions such that the operator does not inhale phosphine.

D.1.5.4.1. Application to Bagged Commodities under Gasproof Sheets

Metal phosphide pellet or tablet preparations should be applied to bagged commodities immediately after the fumigation sheets are placed over the stack and before they are sealed completely to the floor or floor sheet.

When fumigating bagged commodities under gasproof sheets, tablets or pellets should be spread out on trays or sheets of kraft paper so that residual material can easily be collected at the end of the fumigation. *Tablets or pellets should never be piled on top of one another.* The trays containing tablets or pellets should be placed at the base of the stack.

Strings of sachets or blankets containing sachets should be draped at intervals over the stack immediately before it is sheeted over, care being taken not to pile one sachet on top of another.

D.1.5.4.2. Application to Sealed Bag Stacks

When fumigating sealed bag-stacks, the tablets or pellets should be spread out on trays or sheets of kraft paper, so that the residual material can be easily collected at the end of the fumigation. *Tablets, or pellets, should never be piled on top of one another.* The trays containing tablets or pellets should be placed at the base of the stack under the dunnage, through slits cut in the cover after pressure testing has been carried out. The openings are then sealed.

D.1.5.4.3. Application to Bulk Grain Being Loaded into a Vertical Silo

Before commencing the application of tablets or pellets to grain being loaded into a vertical silo, the fumigator-in-charge should ascertain from the management the time that it will take to fill the bin. For example, a 2000 tonne silo bin being filled at an in-loading rate of 150 tonnes per hour will take over 13 hours to fill, but if this is done in 8-hour shifts it will be almost 2 days before the bin is filled. Hydrolysis of tablets and pellets commences immediately they are added to grain and peak concentrations will occur in a bin between 24 and 48 hours. Therefore, in the foregoing example, high concentrations of phosphine will be present in the bin by the following morning and some of the phosphine will be displaced from the bin when in-loading resumes. This situation should be avoided if possible, but if it cannot, *the application rate on the first day could be increased slightly to allow for the loss on the second day and the atmosphere above the bin should be carefully monitored by the fumigator-in-charge during the second day.* It is also important from the foregoing example to ensure that there will be a continuous supply of grain so that the expected in-loading rate can be maintained.

Tablets, pellets, and sachets may be added by hand to the grain stream 'feeding' a silo bin provided that the operator engaged in this work is in a well-ventilated area. Care must be taken to ensure that the correct dose is applied and that applications of the individual formulations are made at regularly spaced intervals. Pellets may be added from an automatic dispenser calibrated to deliver a dosage appropriate to the rate of loading of grain into the bin. This method has the advantages over manual application of reliably spacing delivery and of eliminating the need to station an operator close to the fumigation area. *In the case of a vertical bin, it is most desirable to apply pellets, tablets or sachets to the grain at a point in the conveyor system between the elevator head and the bin.* This eliminates the problems which might be associated with a breakdown of the elevator when a preparation has been applied at or before the elevator boot. If this precaution is not observed, and an elevator carrying grain which has just been dosed breaks down, repairs must be effected under the direct supervision of the fumigator-in-charge, who should frequently monitor the atmosphere of the work space to check that conditions are safe. It may prove necessary to remove the dosed grain from the elevator, and this should be done by the fumigator-in-charge and an assistant, both wearing self-contained breathing apparatus; under these circumstances the fumigator-in-charge must issue a clearance certificate for areas into which phosphine escaped before non-specialist personnel are permitted to resume work.

In well sealed silo bins phosphide preparations can be added to the grain surface after the bin is filled. This avoids the need for continuous addition during filling and permits the removal of the residue of the spent formulation after the treatment is complete. Where the height-to-width ratio of the bin exceeds 2:1, it is necessary to recirculate the bin atmosphere to provide adequate fumigant distribution. Recirculation should be carried out with a fan generating less than 10 kPa differential pressure and having a blade tip speed of not more than 40 m/sec to avoid producing conditions under which the phosphine may ignite or explode.

D.1.5.4.4. Application to Grain Stored in a Horizontal Bulk

Aluminium phosphide tablets (on trays to retain spent residue) may be placed on the grain surface. Similarly, blankets may also be placed directly on the grain surface. Care should be taken to ensure that formulations are never placed on top of one another as excessive heating may occur, increasing the risk of fire.

Aluminium phosphide tablets may also be probed into a bulk of grain but the dosage must be evenly spread throughout the grain mass. The probing pattern must be decided in advance by the fumigator-in-charge. Upon completion of the application of tablets, the surface of the grain should be covered with gasproof sheeting.

However, if the horizontal storage is gastight, the entire contents of the storage should be fumigated without the gasproof sheeting.

Where gasproof sheeting is used to cover the grain in a shed with a leaky headspace, the fabric of the building should be treated by spraying or fogging immediately the sheets are applied. During this operation, the atmosphere in which the spraying or fogging team is operating should be monitored by the fumigator-in-charge.

D.1.5.4.5. Space Fumigation

Space fumigation describes the practice of fumigating empty or substantially empty storages or buildings. Tablets or pellets should be spread out on trays or sheets of kraft paper so that residual material can easily be collected at the end of the fumigation. *Tablets or pellets should never be piled on top of one another*. The trays containing tablets or pellets should be evenly distributed throughout the space.

Strings of sachets, or blankets containing sachets, should be draped at intervals through the building *care being taken not to pile one sachet on top of another*.

Metal phosphide plates or bubble packages containing pellets or tablets can also be used for this application and should be distributed evenly throughout the building.

D.1.5.5. Dosage Rates and Exposure Periods

D.1.5.5.1. Factors Governing Dosage Rates and Exposure Periods

The principles and practical requirements of effective phosphine fumigation upon which dosage recommendations have been based may be summarised as follows:

- The objective of fumigation must be to achieve complete kill of all stages of all species of pests. This will prevent selection for resistance.
- Phosphine should be used in structures in which the standard of gastightness is consistent with a decay of an excess internal pressure from 500 Pa (2" water gauge) to 250 Pa (1" water gauge) in not less than 5 minutes in filled structures of 300–10 000 tonne capacity. Porous surfaces must be sealed, and all seams, cracks, or holes must be filled either permanently (e.g. in the walls or roof) or temporarily (e.g. intake or outlet valves, doors, windows, or hatches). The roofs of silos or other structures sealed to this standard must be painted white to reduce thermal expansion of the atmosphere within the headspace. Apart from reducing fumigant loss, this is necessary to ensure that moisture migration into the headspace and subsequent condensation is minimised. Other outside surfaces of sealed structures should also be painted white.
- Survival of insects in pockets of low concentration of phosphine due to leaks will become increasingly significant with loss rates greater than those inherent in the foregoing gastightness standard and increased dosage rates *will not* compensate for higher loss rates.
- Dosage rates should be aimed at killing the most tolerant stage of the most tolerant species (pupae of *Sitophilus granarius*).
- A minimum fumigation period of 7 days is necessary at temperatures above 25°C:

  – to ensure complete decomposition of aluminium phosphide; and

  – because of the time-dependent nature of the response of *Sitophilus granarius* pupae to phosphine.

  Note also that complete decomposition of the aluminium phosphide from sachets may take appreciably longer than 5 days if the humidity is low.

- The proposed levels of gastightness will require positive steps to ventilate a structure after fumigation. Provision for two openings in the structure (temporarily sealed) must be made during the preparation for fumigation so that a flow-through draught can be provided for ventilation. Wherever possible, a forced draught from a suitable flashproof fan should be used.
- Insect infestations greatly accentuate moisture migration. Thus, structures sealed to the specified levels of gastightness should not be left for long periods before fumigation. However, once the infestation has been controlled and the fumigant removed according to the ventilation procedures, the structure may be resealed. In this state the structure should be virtually insect-proof. *Nevertheless, where prolonged storage is required regular inspections of the grain should be made.*

  In these circumstances operators should be made aware that the atmosphere within sealed structures may contain higher than normal levels of carbon dioxide. Appropriate safety procedures should be followed by persons entering such structures.

D.1.5.5.2. Units of Dosage

Dosage rates are frequently expressed in terms of tablets per tonne. This requires an appropriate conversion when other formulations such as pellets or sachets are used. Another approach to dosage rates is to express them in terms of grams of phosphine per tonne. This applies to all formulations but still requires conversion to the particular formulation chosen. Either method, however, is based on a quantity of fumigant per weight of commodity. This is a satisfactory approach only when the silo, shed, or other structure is either full, or to be filled, with virtually no headspace remaining. In all other situations where there is a substantial headspace, it is necessary to allow for this free space when calculating the total dosage required. However, the dosage in the free space need not be as high as that within the commodity since there is no appreciable loss due to sorption within the free space. Thus, the dosage required can be calculated either on the basis of the internal volume of the structure, or by adding to the commodity dosage sufficient fumigant to allow for the space above or around the commodity. Alternatively, the commodity may be fumigated by placing plastic sheets directly over it, thus eliminating the headspace. Commodity dosage rates may then be used. Generally however, this approach is not recommended since insects are rarely confined to the commodity and those outside the commodity, e.g. in residues elsewhere in a shed, will reinfest the commodity soon after the sheets are removed.

It is essential, in calculating the dosage required, to make allowance for the headspace, in order to ensure an adequate concentration throughout the fumigation enclosure. The recommended method for practical purposes, is to calculate the dosage on the basis of the internal volume of the structure to be fumigated. Consequently, dosage rates for phosphine fumigation are expressed primarily in grams per cubic metre (g/m^3). A rate of 1.5 g/m^3, for example, is approximately equivalent to 2 g/tonne using a grain stowage factor of 1.24 m^3/tonne. However, it should be noted that, because of the exclusion volume of grain, leakage, and sorption, the application rates do not indicate the maximum concentrations of phosphine that will occur within a grain mass.

The following equivalents, based on commercial formulations containing aluminium phosphide as the phosphine source, are given to simplify dosage calculations:

1 g of phosphine = 1 tablet = 5 pellets = 1/11 sachet

These equivalents are for the formulations readily available from recognised agricultural chemical companies and their agents at the time of publication of this document. Read the label of the formulation to be used, in order to ensure that the correct dosage is applied.

D.1.5.5.3. Application Rates and Exposure Periods

The rates given in Table D1 are based on the application of phosphine to gastight structures. *Adding extra tablets or pellets will not compensate for poor standards of gastightness. While higher average concentrations may be achieved, they will not offset the survival that will occur in pockets adjacent to leaks allowing ingress of air and hence dilution of the phosphine.*

Notes on the recommended application rates and exposure periods follow.

- The foregoing recommendations may be applied to raw cereal grains including barley, maize, millet, oats, paddy, brown and milled rice, rye, sorghum, triticale, wheat; pulses; other food commodities such as flour and other ground cereal products, breakfast cereals, dried fruits, dried vegetables and other dried foods, peanuts, oilseeds, cocoa and coffee beans; seeds for propagation; stock feeds; tobacco; empty warehouses and other buildings.
- No attempt should be made to fumigate with phosphine when commodity temperatures are less than 15°C or when grain moisture contents are less than 9% or the relative humidity within the structure or commodity is less than 25%. To avoid sorption, moisture migration, and condensation problems, grain with a moisture content above 16% should not be fumigated.
- No attempt should be made to apply phosphine using surface application methods unless the structure is gastight.
- No attempt should be made to recirculate phosphine unless low flow rate fans of the correct specification are used and unless the structure is gastight. Fans should have a blade tip speed of less than 40 m/sec and should generate a differential pressure of less than 10 kPa.
- Dosage rates (g/m^3) are based on the internal volume of the structure and apply equally to full, part-filled, or empty structures.
- The application of phosphine-generating preparations should be completed in the shortest time possible.
- Where the height to width ratio of the store exceeds 2:1 and the capacity exceeds 300 tonnes, some method of assisted distribution of the phosphine is required (e.g. recirculation) when a surface-application technique is used.
- The recommended exposure period should be considered to commence at the time of completion of fumigant application.
- The fumigation area must be isolated for the entire duration of the exposure period and until a clearance certificate is issued by the fumigator-in-charge.
- If the premises can be locked up they may be left in that condition without supervision during the exposure period; otherwise a watchman must be on duty at all times to prevent unauthorised entry into the fumigation area.

Table D1. Dosage rates for phosphine

Temperature (°C)	Dosage rate (g/m^3)	Equivalent commodity dosage* (g/tonne)	Minimum exposure period (days)	
			Admixture & recirculation	Surface application
Above 25	1.5	2	7	20
15–25	1.5	2	10	20

* Rate appropriate for raw, whole cereal grains. Commodity dosage rates should be used only when structures are full or have little or no head space remaining.

D.1.5.6. Clearing the Fumigant on Completion of the Exposure Period

D.1.5.6.1. Opening the Fumigation Enclosure

At the conclusion of the exposure period, fumigators wearing approved respiratory protection should open up the fumigation enclosure, i.e. remove sheets from bag stacks, open doors or windows of godowns, remove the covers over cell tops or grain surfaces etc., and, if the store is equipped for aeration, open or unseal the inlet ducts and start the fans.

D.1.5.6.2. Ventilation Periods

Minimum periods of ventilation after completion of fumigation are as follows:

Structures containing treated commodities

- With flow-through ventilation and a forced draught provided by a suitable flashproof fan operated either continuously or on a cycle of 2 hours on and 2 hours off for 12 to 24 hours depending on the size of the structure.
- With flow-through ventilation and natural draughts, e.g. wind: 2 to 5 days depending on the size of the structure.

Empty buildings

- With flow-through ventilation and a forced draught provided by a suitable flashproof fan operated either continuously or on a cycle of 2 hours on and 2 hours off for 24 to 48 hours depending on the size of the structure.

• With flow-through ventilation and natural draughts, e.g. wind: variable, depending on the size of the building, the size of the openings, and the velocity of prevailing winds but not less than 48 hours.

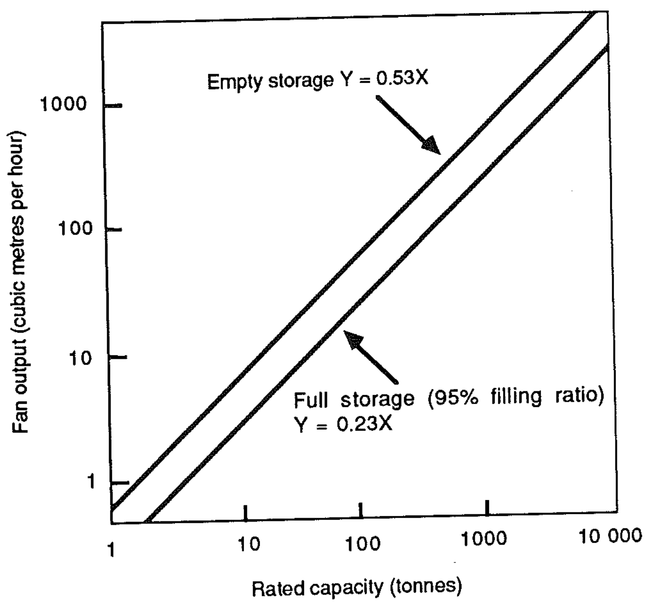
Bag stacks

Following removal of plastic fumigation sheets, a minimum of 12 hours ventilation should be allowed.

Note: all the foregoing ventilation periods are suggested as guides only. Clearance as safe must be made on the basis of appropriate tests and in accordance with the procedures and standards prescribed by local health authorities.

Wherever possible forced draught ventilation should be employed, using a suitable flashproof fan. The size of the fan required to provide 0.4 air changes per hour, a suitable rate, is given in Figure D1.

Fig. D1. Fan output required to give 0.4 air changes per hour, as a function of storage size.



D.1.5.6.3. Testing Fumigant Clearance

When preliminary ventilation is complete, the atmosphere in which men will work must be tested by the fumigator-in-charge check if they can safely enter. The tests should be thorough and systematic. When the fumigator-in-charge is satisfied that work can safely be resumed in every part of the premises, he should issue a clearance certificate to that effect. An appropriate format is given as Appendix 4 to these recommendations.

Where undischarged treated grain is to be removed from a flat-bottomed cell, the atmosphere of the cell must be tested by a trained fumigator and a clearance certificate issued before grain handlers are allowed to enter the space. The fumigator should wear an approved respirator while performing these tests.

D.1.5.7. Post-Treatment Action

Warning signs should be removed. When the treatment has involved the direct addition of phosphide preparation to the grain, a cautionary notice, in the local language(s), should be placed on all access hatches to a store which contains treated grain stating:

FUMIGATED WITH PHOSPHINE
(Date of Completion of Treatment)
PHOSPHINE MAY BE EVOLVED FROM RESIDUAL POWDER WHEN THIS GRAIN IS DISTURBED

These notices should be removed or cancelled when the treated grain is unloaded. Residues of tablets or pellets, where they can be collected, and spent sachets, blankets, or plates should be disposed of in accordance with manufacturers' recommendations.

D.1.5.8. Record Keeping, Including Assessment of Effectiveness of Fumigation

The fumigator-in-charge must maintain a written record of each fumigation. The record must include:

• the names of all personnel engaged either on grain handling or fumigation work during the application of fumigant, and the nature of their duties

• the location of the treatment

• type of storage—bag, bulk, container

• type and tonnage of commodity treated*

• volume of enclosure*

• results of gastightness test*

• the date and time of commencement of fumigant application*

• the dosage used (expressed preferably in grams per m^3 or tablets, pellets, or sachets per tonne) and exposure time*

• length of airing period*

• time of issue of declaration of clearance*

• a declaration that the actual dosage applied was equal to the target dosage, and that all packaging materials that had contained the fumigant formulation had been cleared and accounted for prior to supervised disposal

• when sampling lines were installed, records of all measurements of concentrations obtained from within the fumigation enclosure

• details of any incidents or accidents.

Items marked with an asterisk should also be recorded on stack/bin cards.

D.1.5.9. Fumigation Failure

In the event of fumigation failure, every effort must be made to determine the cause of the failure. Inadequate gastightness of the structure is frequently the cause. Before attempting further fumigation with phosphine, this or any other deficiency must be rectified. Alternatively, other treatments should be used. Higher dosage rates of phosphine *will not* compensate for poor gastightness.

D.1.6. First Aid

No-one should enter an area under fumigation except in extreme emergency and then only with adequate respiratory protection.

Any person who appears to have been affected by phosphine must be taken at once into fresh air, kept quiet and warm, and medical attention should be obtained. If breathing stops or shows signs of failing, resuscitation must be commenced immediately.

There is no specific antidote.

DO NOT administer any milk, butter, oils (e.g. castor oil), or alcohol.

D.1.7. Witholding Period

Allow a period of 2 days after ventilation has been completed before using treated commodities for human consumption or for stock feed.

Treated commodities may be transported safely after completion of the recommended ventilation period.

D.2. Methyl Bromide

D.2.1. Objectives and General Requirements

The following code is designed to establish the principles for effective fumigation with methyl bromide. These principles cover both safety and efficacy. Operational procedures incorporating them, applicable to specific types of fumigations, are given in the additional parts of the recommendations relating to methyl bromide.

Methyl bromide fumigations are carried out to eradicate pests and other unwanted organisms from commodities and storage enclosures, particularly where short exposure periods are required. They may also be specified as a treatment in certain quarantine situations.

An enclosure is required around the commodity. It must be well sealed, preventing both loss of fumigant and hazard to humans. Methyl bromide is introduced into the enclosure, either as a liquid or gas, and is either distributed by some form of forced draught or allowed to disperse naturally throughout the enclosure. The design of the fumigation enclosure and fumigant application and dispersion system should be such that an even concentration of methyl bromide is achieved throughout the enclosure soon after application. After an adequate exposure regime has been achieved, typically in about 20 hours, the fumigant must be vented from the enclosure safely and to a level where subsequently it poses no hazard.

Although methyl bromide is a versatile fumigant in very common use, it can produce adverse effects in commodities. If definitive information regarding its effects on a particular commodity is not available, its influence should be tested on a small scale before it is used widely to treat that commodity.

Methyl bromide can cause taint on both wheat flour and whole grain if applied incorrectly. In particular, liquid methyl bromide, or excessive or repeated treatments can taint flour (presumably from formation of volatile sulphur compounds through reaction with sulphur-containing grain constituents). Slight 'staleness' has been found in freshly baked rolls from flour of wheat that has undergone multiple methyl bromide fumigations. Wrapping of bread made from flour repeatedly fumigated with methyl bromide may help retain the smell that can be detected in the freshly baked loaf. *Soybean flour should not be treated with methyl bromide as it is particularly susceptible to persistent taint.*

Methyl bromide may also affect the processing qualities of grain treated with it, though the evidence on this matter is somewhat contradictory. Studies have found that flour derived from wheat treated with methyl bromide gave a more compressible loaf than flour from wheat treated with other fumigants, and that excessive doses of methyl bromide result in flour with poor bread-making qualities.

Methyl bromide may also react with nucleophiles in grain, usually nitrogen or sulphur containing materials, causing a reduction in the nutritional value of the commodity.

When and when not to use methyl bromide as a fumigant

Methyl bromide should be used:

- when a treatment must be completed within 4 days or less
- for most quarantine treatments

*Methyl bromide use should be avoided:**

- on seed required for planting or malting
- on very absorbent materials, such as expeller cake or oilseeds
- in areas immediately adjacent to workspaces or habitations
- on materials previously fumigated with methyl bromide more than once
- where there is no trained, qualified, and properly protected fumigation team
- in unsealed enclosures

* There may, however, be occasions when methyl bromide *must* be used to fulfill quarantine or contractual obligations, where it would not otherwise be the fumigant of choice.

D.2.2. Methyl Bromide as a Fumigant

D.2.2.1. General Characteristics

Methyl bromide is a colourless, odourless, nonflammable gas at normal temperatures. It liquefies easily under pressure and is supplied and stored as a liquid under pressure.

The basic properties of methyl bromide are as follows:

formula	CH_3Br
molecular weight	95
boiling point (°C)	3.6
specific volume at 30°C, 1 atm (m^3/kg)	0.256
specific gravity (gas) [air = 1.0]	3.40
gas density at 30°C, 1 atm (kg/m^3)	3.908
vapour pressure at 30°C (atm)	2.5
conversion factor, g/m^3 to ppm (30°C, 1 atm)	260
flammability limits in air (% v/v)	13.5–14.5
solubility in water (v/v)	3.4
specific gravity at 30°C, 60% R.H. (liquid, kg/L)	1.7

Methyl bromide is chemically reactive and may combine with and alter the properties

of the constituents of many articles that may normally be subject to fumigation. Notably, methyl bromide reacts with sulphur-containing molecules such as are found in natural rubber and feathers. Methyl bromide will form an explosive material with aluminium in the absence of oxygen; aluminium tubing should thus never be used to dispense methyl bromide. Liquid methyl bromide is a powerful solvent. It will dissolve bituminous materials and will cause softening and swelling of some plastics, notably flexible PVC.

D.2.2.2. Adverse Effects on People

Methyl bromide is extremely toxic and there are many cases of poisoning, some fatal, on record. Methyl bromide is particularly dangerous as it is both hard to detect and signs of poisoning may not be apparent until several hours after exposure. Thus, without proper precautions, persons may continue to expose and further endanger themselves unaware that all is not well.

There is no recognised, specific antidote for methyl bromide poisoning. However, it is said that large oral doses of cysteine are beneficial.

Methyl bromide can cause:

- damage to the brain and nervous system and possibly the kidneys;
- massive accumulation of fluid in the lungs (oedema); and
- severe burns and blistering of the skin.

The effects of exposure to the gas depend on the concentration, and on the period and frequency of exposure. Harmful effects may result not only from exposure to a high concentration, but also from continued or repeated exposure to low concentrations. The recommended limit for occupational exposure to methyl bromide is 5 ppm (0.02 g/m^3) (8 hours time-weighted average) and 15 ppm (0.06 g/m^3) short-term exposure limit (10 minutes time-weighted average). At concentrations of the order of 1% (10 000 ppm) in air by volume (approx. 40 g/m^3) the presence of the gas may be detected by irritation of the eyes and nose. The effects of an exposure of only a few minutes at this concentration may include headache, soreness of the eyes, loss of appetite, and abdominal discomfort. These symptoms may then persist for several days. There may also be numbness of the feet, and disturbance of sensation in the legs may persist for several months. After exposure for a longer period, death is likely to ensue within 48 hours due to massive accumulation of fluid in the lungs (pulmonary oedema).

A person exposed to concentrations much less than 10 000 ppm may not receive any warning signs; exposure may therefore be prolonged. Poisoning has been reported from prolonged exposure to concentrations as low as 35 ppm. Within a short time, the person may feel unwell, suffer headache, smarting of the eyes, and nausea. *These symptoms may be attributed to a trivial illness and ignored, but it is stressed that this is a particularly dangerous situation.* The more serious effects due to damage to the nervous system do not appear until after an interval that can vary from a few hours to a day or so. They consist initially of difficulty in focussing the eyes, incoherent speech, staggering gait, and excitement suggesting drunkenness. There may be weakness of the limbs, especially the legs. This may be followed by fits and unconsciousness and, if so, the prospect of recovery is very bad. If the victim survives, it may be many months or years before complete recovery and during this time, depression, loss of memory, insomnia, weakness, and tremors may occur, and insanity may result.

Skin damage is caused by contact either with liquid methyl bromide or high concentration of the vapour. Clothing, shoes, rubber gloves, surgical dressings, etc. can be penetrated by methyl bromide and, unless such coverings are removed, vapour may remain in contact with the skin for a long time, causing severe blistering. The blisters are usually large and surrounded by areas of redness and swelling and may take a long time to heal.

D.2.2.3. Adverse Effects on Commodities

As noted previously, methyl bromide can cause adverse effects on many commodities. The effects include:

- loss of germination
- formation of residues
- taint
- change in processing quality.

Loss of Germination. Treatment with seeds can lead to loss of germination and germination vigour. The tolerances of different seeds vary greatly, but many are quite affected by even a single treatment at normal dosages. Where methyl bromide must be used on seed for planting or malting a reduced dosage should be used (e.g. 10 g/m^3).The effect of methyl bromide on germination is exploited in its use to control weed seeds in seed beds, potting mixtures, etc., and as a quarantine treatment to destroy germination.

Formation of Residues. Methyl bromide reacts with –OH, –S–, and >NH groups in commodities forming methylated materials and inorganic bromide. There are tolerances for total inorganic bromide levels in foodstuffs resulting from fumigation (50 mg/kg in cereals). The methylated materials are believed to be of no significance toxicologically. Inadequately aired materials may contain appreciable quantities of sorbed unchanged methyl bromide. This is also subject to a tolerance level (0.01 mg/kg).

Taint. Fumigation of absorbant commodities such as wheat flour, soy flour or nuts, particularly at high dosages, can give rise to a sulphurous taint noticeable especially on processing. Bread baked from fumigated flour, sliced and wrapped soon after baking, often has an unfamiliar smell. The odour is presumably largely dimethyl sulphide arising from the attack of methyl bromide on sulphur-containing materials. A similar reaction can lead to persistent taint in materials that may be treated incidentally in a fumigation. These include feathers, wool, tanned leather, natural rubber, iodised salt, and cellophane.

Change in Processing Quality. Methyl bromide fumigation may alter end-use quality of treated commodities, particularly if excessive dosages are used. There are few data on this subject. However, high dosages of methyl bromide are known to alter baking quality of flour derived from treated wheat.

D.2.2.4. Detection and Measurement of Methyl Bromide

The apparatus used for measurement of methyl bromide depends on the situation and concentration present.

Insecticidal Concentrations (greater than 4 g/m^3). At concentrations encountered during effective fumigations, methyl bromide can be measured in the field using either an interferometer (e.g. Riken) or a thermal conductivity meter (e.g. Fumiscope). Both instruments are battery-operated and portable. They can be bought already calibrated for methyl bromide. It is important to maintain the absorbers in these instruments correctly. The absorbers remove water vapour and CO_2. If they function incorrectly the readings from the meters are erroneous and high.

Health Limit Concentrations (0.01–0.2 g/m^3, 2–50 ppm approximately). Concentration in air in the range of the TLV can be measured either by indicator tubes (Dräger, Gastec, etc.) or less accurately using a halide lamp (several manufacturers). Portable electronic detectors are also available. The colours of flame given by the halide lamp vary with methyl bromide concentration. If the flame has a light green edge then there is about 20 ppm CH_3Br present. More intense green shows higher concentrations are present. Note that the halide lamp cannot be used in atmospheres containing dust or flammable vapours because of fire and explosion risk. The lamp must be maintained carefully if it is to indicate correctly. The indicator tube system is safer, but more expensive, slower and difficult to use. Two different tubes in series are used. The manufacturer's instructions must be followed exactly.

Residues (greater than 5 mg/kg for Br^-; greater than 0.01 mg/kg for CH_3Br). Unchanged methyl bromide residues can be estimated by head space chromatography using a flame ionisation detector. Bromide in residues is best estimated by X-ray fluorescence. Both methods must be carried out in a laboratory.

Note that methyl chloride may be produced during treatment of commodities with methyl bromide. Interferometers and most electronic devices do not distinguish between these two compounds and may thus indicate somewhat higher methyl bromide concentrations than are truly present, particularly late in a treatment and during airing.

D.2.2.5. Warning Agents

Methyl bromide is sometimes supplied containing a small quantity of a material readily detected by smell to act as a warning agent. This can permit a leak of the odourless methyl bromide gas to be detected in some circumstances. The lachrymal (tear gland stimulating) agent, chloropicrin, and the sweet smelling amyl acetate have been used as warning agents. These agents are particularly useful in situations where methyl bromide may leak from storage vessels. However, *they do not provide* an indication of leakage from a fumigation enclosure as the agents are highly sorbed by most commodities. Note that the use of chloropicrin at 2% w/w increases both the inhalation hazard and phytotoxicity when used with methyl bromide and may itself cause residue problems.

D.2.3. Personal Protection

D.2.3.1. Respiratory Protection

Fumigators and other persons at risk from inhaling excessive quantities of methyl bromide must be provided with either a full-face canister respirator or an open-circuit, self-contained breathing apparatus with full face mask. Respiratory protection must be worn whenever tests of the atmosphere reveal concentrations of the gas greater than the hygienic standard, currently 5 ppm in many countries.

Masks and canisters should be issued on a personal basis and a register of use maintained by the fumigator-in-charge.

D.2.3.1.1. Canister Respirators

Canister respirators should be fitted with a canister designed for protection against methyl bromide, as recommended by occupational health authorities. Each time a respirator of this type is put on, the facial fit should be tested by closing the inlet to the canister with the palm of the hand and inhaling deeply; the vacuum so created should cause the facepiece to adhere to the face for about 15 seconds.

With this type of respirator it is essential that the canister be used within its stated shelf life. The respirator canister must always be replaced before either its shelf life has expired or the recommended usage time has been reached. The expiry date of a canister may easily be calculated since each is marked with the date of manufacture and shelf life.

Canisters should be stored in a cool, dry, well-ventilated place away from contamination by any fumigants. The following precautions should always be observed:

- When the canister is attached to the respirator facepiece after the top seal is removed, record the date. This is best done by writing the date on a small adhesive label which must be affixed to the canister. This label should also be used as a 'log' to record exposure of the canister to the fumigant.

- Before using the respirator, remove the cap and the seal over the air inlet valve of the canister. Again, at this time mark the date on the 'log' label. Once this seal is removed, even if there is no exposure to fumigant, replace the canister after a lapse of 6 months.

- After any fumigation in which there has been prolonged exposure to low concentrations of the fumigant or accidental exposure to high concentrations, immediately discard the canister. *As a guide, 1 hour of wearing is the usual period after which a canister should be discarded.* This could be extended to 2 hours, but only when exposure is minimal. Allow a wide margin of safety in estimating exposure times as canisters cost little in terms of health of the individual. If there is any doubt about the exposure life of the canister, discard it.

- Canisters should be resealed with the original top and bottom seals between uses.

- When canisters are discarded, they should be rendered unusable by mutilating the inlet port and disposed of under conditions which will prevent them from being picked up and used again.

- Canisters that show any sign of external damage must be considered worthless, and should be discarded. A severe blow on the metal covering may cause displacement of the contents, permitting contaminated air to pass through to the wearer.

- Immersion of the canister in water renders it useless. Water may enter the canister through the facepiece. Disconnect the hose and canister when cleaning or disinfecting the facepiece.

D.2.3.1.2. Self-contained Breathing Apparatus

Self-contained breathing apparatus is to be preferred wherever this equipment is available. The facial fit of this type of apparatus may be tested in a manner similar to that employed with the canister respirator, except that the cylinder valve is closed prior to deep inhalation.

D.2.3.2. Skin Protection

A cotton boiler suit (coverall), with full arms and buttoned at the throat, should be worn by all persons engaged in a fumigation. Impervious gloves and footwear should also be worn. Any protective clothing, including footwear, subjected to liquid methyl bromide should be discarded after allowing to air in a safe, well-ventilated place.

D.2.4. Fumigation Personnel

D.2.4.1. Minimum Number of Persons.

Treatment of enclosures of up to 10 000 m^3 capacity shall be performed by a gang of not less than three (3) qualified and experienced fumigators. One of these people should always be designated as the fumigator-in-charge (see next section). An additional person is required for each additional 5000 m^3 of volume to be fumigated.

D.2.4.2. Qualifications of Personnel

At least one member of the work force employed in each fumigation should be designated fumigator-in-charge and be given responsibility for the safe and effective execution of the work. The fumigator-in-charge must hold (where applicable) a licence to fumigate with methyl bromide. He should have a minimum of two years active involvement in the fumigation of structures and/or stored products with methyl bromide and a detailed knowledge of fumigation practice. He must be present at all times during the active phases of each fumigation. In addition to the organisation and supervision of the work of his subordinates, his duties should include:

- the planning of the fumigation and the procurement of materials and equipment;
- the thorough instruction of his subordinates with respect to safety precautions, the maintenance and correct use of protective equipment, the general work plan, and individual tasks;
- the performance of tests for gastightness and for the fumigant gas and the issuing of clearance certificates.

The other fumigators in the gang should hold a fumigation licence and have some experience in the general practice of fumigation. Persons without fumigation experience may be employed as fumigators' assistants *provided that they are trained in advance of treatment,* with emphasis on the properties and hazards of methyl bromide, fumigation procedure, the use and maintenance of protective equipment, and first aid measures.

D.2.4.3. Monitoring Health of Operators

Where staff are part of a regular fumigation team, *the fumigator-in-charge should ensure that regular health checks are performed on himself and all members of the team.* This should be done in consultation with and according to the requirements of local health authorities.

D.2.5. Fumigation Practice

D.2.5.1. Formulation

Methyl bromide is supplied as a liquid under its own vapour pressure, either in steel cylinders or cans. Cans contain 0.7 kg of methyl bromide with 2% chloropicrin. Cylinders may contain up to 100 kg with or without warning agent. Cylinders may or may not be fitted with an eductor tube. This tube runs from the valve to the bottom of the cylinder and allows liquid methyl bromide to be run from the cylinder under pressure.

D.2.5.2. Storage and Handling of Formulations

Methyl bromide stocks should be stored in a dry, well-ventilated, and locked enclosure at least 25 m from habitation and domestic animals and 10 m from work places. The key of the store should be held by a designated person responsible for its safe keeping and the conduct of the store. The store must carry a warning sign

on the door signifying presence of poison gas. Access should be restricted to nominated and responsible staff equipped with respiratory protection.

Cylinders and particularly cans can become rusty and unsafe if stored poorly. The total contents can leak out. Stocks should be inspected periodically (less than 3 month intervals). Containers showing signs of deterioration should be removed from the store at the earliest opportunity and the contents vented in the open air in a safe place.

Cylinders and cans should be transported only in well ventilated cargo areas outside the passenger compartments. Respiratory equipment should be available to persons involved in transport of methyl bromide. They should be trained in its use and aware of the hazards of methyl bromide in case of an accident.

D.2.5.3. Preparation for Fumigation

D.2.5.3.1. Planning

Before commencing a treatment, the fumigator-in-charge should prepare a plan describing the intended course of the fumigation. He should explain this plan in detail to persons involved in the fumigation, allocating responsibilities for particular aspects of the plan where appropriate. The plan should include how the fumigant is to be applied, how the enclosure is to be sealed, how the fumigant is to be vented after the treatment, at what times the various actions involved in the fumigation are to be carried out and who will carry them out. If forced mixing is required, the required fans and duct work must be in place. The piping— copper or Alkathene (a type of plastic; registered trade name of the ICI company) only— carrying fumigant to the enclosure must be designed so that no liquid methyl bromide comes into direct contact either with foodstuffs or other absorbent commodities.

D.2.5.3.2. Notice of intention to fumigate

An authorised fumigator intending to fumigate a building or other enclosed space shall deliver a notice in writing 24 hours prior to the fumigation commencing in the form of Schedule No. 1 (see Appendix 2) to:

- the appropriate authority;
- the nearest Police Station and Fire Brigade; and
- every tenant or occupier within the fumigation and risk area who must acknowledge receipt by signing the duplicate copy which shall be retained by the fumigator.

D.2.5.3.3. Definition of risk area

There is a risk area around a fumigation enclosure comprising all adjacent spaces in which harmful concentrations of the fumigant might, in the opinion of the fumigator-in-charge, become present. The risk areas may be entered only by permission of the fumigator-in-charge. It should be conspicuously marked to warn people not involved in the fumigation operation not to enter the area. Warning notices must display the identity of the fumigant and the name and address of the fumigator-in-charge, together with emergency telephone numbers. Special care should be taken over buildings or rooms with walls common to an area that is to be fumigated. Leakage into such spaces can often occur. They are thus normally included in the risk area. Where necessary, the fumigator-in-charge should take possession of any keys to doors in the fumigation and risk areas.

D.2.5.3.4. Sealing of the Enclosure

The enclosure in which the fumigation is to be conducted must be made as gastight as practicable. Methods of sealing and testing for gastightness are given in Appendix 5 and, in more detail, in the separate parts of these recommendations giving operational procedures for specific applications. (Any fumigation using forced recirculation or carried out within 30 m of a workspace or habitation and involving more than 10 kg of methyl bromide shall be carried out in an enclosure meeting a pressure test where a pressure halving occurs in not less than 5 minutes.) Fumigation sheets, where used, must be intact, free from holes and tears. They must be joined by the roll and clamp system.

Bag stacks to be fumigated should be constructed on top of a gas-proof ground sheet or on an impervious floor e.g. a concrete floor painted with a sealing paint. Cover sheets should be undamaged and sealed to the ground sheet.

D.2.5.3.5. Ventilation of Adjacent Areas

Preparation for the ventilation of areas adjacent to the treatment enclosure must be made before introduction of the fumigant. Enclosed areas adjacent to a fumigation enclosure must be subject to forced ventilation at not less than 1 air change per hour throughout the treatment until the fumigation area is declared free of gas. Areas adjacent to a fumigation may continue to be used for normal working activities provided the fumigation enclosure meets a 5 minute decay time pressure test and an automatic monitoring system is installed that sounds an alarm if the hygienic standard is exceeded. Open areas adjacent to a fumigation and under natural ventilation should be entered only by personnel with respiratory protection.

There should be good ventilation, artificial if necessary, at the point from which the operators apply the fumigant.

D.2.5.3.6. Warning Signs and Precautions to Prevent Entry

The fumigator-in-charge of the fumigation of any building, vessel, or enclosed space shall, immediately before the application of fumigant, affix a warning notice to each door and other means of access to the fumigation area. These notices should have a warning symbol appropriate to the country/culture concerned and have printed on them, in the local language(s), the following English text:

DANGER–KEEP OUT
POISON GAS
FUMIGATION WITH METHYL BROMIDE

The notices should have a white background and the printing should be in capital letters not less than 10 cm (3 inches) high, in a colour that stands out from the background.

The authorised fumigator's name, contact address, and telephone number must be clearly shown at the foot of the notice. The form of notice suggested is shown in Appendix 3.

All warning notices must be suitably illuminated at night.

If possible, preparations must be made to lock or bar all access points to the risk area. Two watchmen should be present at the start of the fumigation and should remain on site, *outside the risk area,* throughout the treatment, to ensure unauthorised and unprotected persons do not enter the risk area.

D.2.5.3.7. Final Safety Checks

No person shall commence to fumigate any building or other enclosed space until:

- The fumigator-in-charge has personally checked all portions of the fumigation area and risk area to ensure that no persons or domestic animals remain therein. Immediately after this inspection, the fumigator-in-charge will ensure all access points are closed and fumigation warning notices are in place.
- All fires and naked lights within the fumigation area have been extinguished and all oil, gas, and electricity supplies have been turned off at the mains. They shall remain off until the clearance certificate has been issued.
- All liquids and foods which are liable to absorb the fumigant have been removed from the fumigation area.
- All windows and ventilators *in the risk area* have been opened to provide maximum ventilation.
- Fans as required are in position and tested for efficiency.
- The nearest telephone has been located and its number noted.
- It has been confirmed with Police and Fire Stations that fumigation is about to commence.

D.2.5.4. Fumigant Application and the Holding Period

Methyl bromide should be introduced into the enclosure through suitable pipework and, if necessary, a vaporiser (for coverting liquid fumigant to the vapour or gas phase) situated outside the fumigation area. Care must be taken to ensure that the correct dosage is applied. All application equipment should be leak-free. Fumigators should wear protective clothing and respiratory protection. At other times, operators may carry respiratory protective equipment 'at the ready', provided the risk area atmosphere has been checked and found to be safe.

A halide lamp or other detector should be used to detect leakages in the application equipment and piping outside the fumigation area, especially at joints and couplings. Any leakages must be corrected by an operator wearing adequate and suitable respiratory and protective equipment before continuing with the fumigation.

In the event of an emergency, for example if a delivery pipe becomes broken or disconnected and a leakage of fumigant is possible, one of the fumigators, wearing adequate breathing apparatus, *should close the main cylinder valve and then withdraw from the risk area.* All other fumigators should withdraw at once. After a period of ventilation a fumigator should check the concentration in the risk area whilst continuing to wear respiratory protective equipment. When the concentration is below the short-term exposure limit he may then carry out the necessary adjustments or repairs.

After application of the fumigant the enclosure should be checked for leaks using a halide lamp or other detector. Leaks down wind may be detected readily, but those up wind may not be indicated as they will not be passing methyl bromide gas. All leaks found should be remedied before the fumigation team leaves the site.

Methyl bromide concentrations in the fumigation enclosure should be monitored at not less than 6–hourly intervals during the holding period, using the gas sampling lines fitted before application of the fumigant.

The fumigator-in-charge and one other qualified fumigator should remain within 15 minutes travelling time of the treatment during the holding period so that they can be alerted by the watchmen and respond promptly to any emergency relating to the treatment.

D.2.5.5. Dosage Rates and Exposure Periods

For normal fumigations, dosage rates and exposure times should be such as to yield a **Ct** product (see Appendix 6) of at least 150 g hours/m^3 at temperatures of 25°–29°C, and at least 100 g hours/m^3 at a temperature of 30°C or above.

For quarantine purposes, the dosage rates and exposure times must be such as to yield **Ct** products that are greater than those for commercial storage. These **Ct** products may need to be very high, e.g. greater than 1600 g hours/m^3 against *Achatina fulica* (African giant snail) and, in the case of grain pests, greater than 400 g hours/m^3 against *Trogoderma granarium.*

Methyl bromide is sorbed appreciably by various commodities and allowance must be made for this in calculating the quantity required to provide a given **Ct** product. The quantity of methyl bromide needed is given by a combination of the space dosage (**S**) and the commodity dosage (**M**) thus:

$$\text{Grams required} = \mathbf{S} \times \text{total volume of enclosure } (m^3) + \mathbf{M} \times \text{tonnage present}$$

using the values in Table D2. These values are given as a guide and should be adjusted in the light of experience based on results of monitoring fumigations and the **Ct** products achieved.

Table D2. Dosage parameters for methyl bromide applications to various commodities for control of insect pests.

Commodity	S (g/m^3) plus	M (g/tonne)	Exposure period (hours)
Paddy, brown and milled rice, barley	10	0	24
Wheat, oats, maize, pulses	10	20	24
Sorghum	10	40	24
Flour, nuts, oilseeds, rice bran*	10	60	48
Oilseed cakes and meals*	10	120	48

* These commodities should not be fumigated with methyl bromide unless required by contractual obligations or for quarantine reasons. Other fumigants are to be preferred.

The required **Ct** product can usually be achieved throughout an enclosure in 18 hours provided the application system is well designed or forced recirculation is used. Adequately rapid distribution can be achieved in small enclosures such as freight containers with only a single point of application.

For quarantine fumigations a 48 hour exposure with 130 g/m^3 of methyl bromide is recommended.

Note that with highly sorptive materials such as oilseeds or with quarantine fumigations a single fumigation may give inorganic bromide residues higher than permitted.

D.2.5.6. Clearing the Fumigant

At the completion of the fumigation period, the fumigation and risk areas should be ventilated.

The initial stages of clearing methyl bromide from a treatment are potentially the most hazardous part of the fumigation process. Respiratory protection must be worn at all times by persons involved until methyl bromide can no longer be detected above the threshold limit value in the free atmosphere around the treated commodity.

The sequence and speed of the clearing operation should be decided by the fumigator-in-charge after considering factors such as the concentration of fumigant within the enclosure, the volume of the storage, wind velocity and direction, and the proximity of inhabited buildings. With large fumigations under sheets, the opening of the seams and removal of sheets should be gradual, with alternate periods of work and ventilation, until concentrations in the stack are low enough to permit safe removal of all sheets. There should be maximum ventilation of the working area, using dispersal fans where possible.

The atmosphere in the risk area and fumigation enclosure should be tested periodically by the fumigator-in-charge until the methyl bromide concentration has fallen below the hygienic standard. Special account should be taken of sorbent materials which may desorb gas for some time after the conclusion of the operations. The fumigator-in-charge should then issue a certificate of clearance (see Appendix 4) when satisfied that the areas are safe for reoccupation. Warning notices should be removed or effectively defaced and barriers removed. Civil authorities notified that the fumigation was to take place, should be informed of its completion.

Vaporisers, piping, and other apparatus associated with the fumigation should be blown out mechanically with compressed air in a well ventilated safe place, before being stored or transported. This is particularly important if the warning agent, chloropicrin, has been used as some of this may condense in the apparatus, providing a serious and unexpected safety hazard if not removed effectively. All fumigation sheets should be aired for not less than two hours before rolling for storage and future use.

D.2.5.7. Record Keeping, Including Assessment of Effectiveness of Fumigation

The fumigator-in-charge must maintain a written record of each fumigation carried out. The record must include:

- the names of all personnel engaged either on grain handling or fumigation work during the application of the fumigant, and the nature of their duties
- the location of the treatment
- type and tonnage of commodity treated
- type of storage—bag, bulk, container
- volume of enclosure*
- results of gastightness test*
- date and time of commencement of fumigant application*
- the dosage applied and exposure time*
- **Ct** product achieved*
- length of ventilation period*
- time of issue of declaration of clearance*
- when sampling lines were installed, records of all measurements of concentrations obtained from within the fumigation enclosure*
- details of any incidents or accidents.

Items marked with an asterisk should also be recorded on stack/bin cards.

Copies should be kept of all notices issued and of clearance certificates. A register of issue and use of protective equipment should be kept.

D.2.6. First Aid

D.2.6.1. Entering Contaminated Area

No-one should enter an area under fumigation except in extreme emergency and only then with adequate respiratory protection. If a person becomes incapacitated in a fumigation enclosure or risk area, rescuers entering must be adequately protected with self-contained breathing apparatus or appropriate canister type respirators.

D.2.6.2. Evacuation of Succumbed Person

The patient should be carried out into the fresh air and laid down.

In the case of an accident, one person should begin first aid treatment while another calls a doctor and ambulance, giving details of gas and circumstances of exposure.

Measures to be taken while awaiting arrival of medical aid

- Apply artificial respiration and cardiac massage if required
- Loosen all tight clothing
- Remove all contaminated clothing, including shoes, socks, underclothes, wrist watch, and spectacles—prolonged contact with contaminated clothing can cause severe skin burns
- Skin decontamination—thoroughly wash contaminated skin with clean water
- Eye decontamination
  - hold eyelids open and wash eyes immediately with a gentle flow of water
  - continue washing until doctor arrives
  - do not use any chemicals, they may increase the injury.

D.2.7. Witholding Period

Allow a period of 2 days after completion of ventilation before using treated commodities for human consumption or for stock feed.

Treated commodities may be safely transported after completion of the recommended ventilation period.

D.3. Carbon Dioxide

The following code is designed to establish the principles for effective fumigation with carbon dioxide. These principles cover both safety and efficacy. Operational procedures incorporating them, applicable to specific types of fumigations, are given in the other parts of the recommendations applicable to carbon dioxide.

Carbon dioxide fumigations are carried out to eradicate insect pests from commodities held in well-sealed storage enclosures of various types, from sheds to freight containers. The method is particularly applicable where long term storage is envisaged, the fabric of the store acting as a physical barrier to reinfestation following an initial disinfestation with the fumigant. Thus, bag stacks of dry commodity held in well sealed plastic enclosures can be safely stored for long periods without deterioration in quality.

D.3.1. Objectives and General Requirements for Effective Fumigation

The objectives of a carbon dioxide fumigation are to maintain toxic concentrations of carbon dioxide long enough to kill the most tolerant stage of the most tolerant species that may be found. In the absence of *Trogoderma* species this means maintaining a concentration of greater than 35% carbon dioxide in all parts of the enclosure for more than 15 days, at ambient temperatures at or above 25°C.

When and when not to use carbon dioxide as a fumigant

Carbon dioxide is the fumigant of choice:

- where long-term storage is planned, i.e. more than 15 days
- where freedom from residues is of value
- where phosphine, methyl bromide, and hydrogen cyanide treatments are not accepted by markets
- where a rapid kill of rodents is desirable and hydrogen cyanide unacceptable
- where treatments must be undertaken close to workspaces and/or habitations

Carbon dioxide should not be used:

- where a treatment must be completed in less than 15 days
- where *Trogoderma granarium* is present
- where seed viability and germination may be affected

D.3.2. Carbon Dioxide as a Fumigant

D.3.2.1. General Characteristics and Chemical Properties

Carbon dioxide (formula: CO_2) is a nonflammable, colourless, odourless gas, about 1.5 times as heavy as air. It is supplied either as liquid maintained by its own vapour pressure (58.3 kg/cm^2 at 30°C), or as solid 'dry ice' subliming at –78.5°C.

Other basic properties of carbon dioxide are as follows:

molecular weight	44
boiling (sublimation) point (°C)	−78.5
specific gravity (gas) [air = 1.0]	1.51
gas density at 30°C, 1 atm (kg/m^3)	1.732
specific volume at 30°C, 1 atm (m^3/kg)	0.548
conversion factor, g/m^3 to ppm (30°C, 1 atm)	560
flammability limits in air	nonflammable
solubility in water (v/v)	0.76
specific gravity at 30°C, 60% R.H. (liquid, kg/L)	0.93

D.3.2.2. Adverse Effects on People and Commodities

The normal concentration of carbon dioxide in air is about 0.03%, the hygienic standard (i.e. the concentration to which a worker may be continually exposed without ill effects) in many countries is 0.5%. Concentrations in the range 2–5% cause a noticeable increase in the rate of breathing, from 5–10% breathing becomes laborious and at 10% it can voluntarily be endured for only a few minutes. Exposure to 12–15% causes unconsciousness, while 25% will lead to death in a few hours.

Recovery from exposure to high concentrations of carbon dioxide is generally complete, with no long term effects on health.

In general there are no reports of quality degradation when carbon dioxide has been applied to dry grains and grain-like commodities (grains, pulses, oilseeds, etc). However, research in this area is limited and has been concentrated so far on wheat, rice (white, brown, and paddy), barley, coffee, and maize. This list is expected to grow. For other commodities and in all cases of seeds for planting, a cautious approach is needed and advice should be sought if maintenance of quality or germination are critical.

D.3.2.3. Detection and Measurement

There are numerous portable robust analytical techniques for carbon dioxide, both for workplace monitoring and measuring concentrations within the fumigation enclosure. The following list, by no means complete, contains some examples of these techniques and some proprietary equipment (the brands are given for information only and the list is neither complete nor an endorsement of specific products):

• Gas detector tubes (Dräger, Auer)

• Interference refractometer (Riken)

• Volumetric (Fyrite)

• Thermal conductivity (Gow Mac)

D.3.3. Personal Protection

D.3.3.1. Respiratory Protection

As a general rule, respiratory protection is not needed in the routine conduct of carbon dioxide fumigations. Concentrations are unlikely to reach dangerous levels in unconfined spaces at or above ground level. However, localised areas below floor level or small enclosed working spaces around the fumigated structure could contain dangerous levels of carbon dioxide. It is also possible that inadequately ventilated and aired gastight fumigation structures after a fumigation is complete will become hazardous as carbon dioxide is desorbed.

As carbon dioxide poses a threat to life and health only at significant concentrations canister type gas-masks are not appropriate. Where access to an area with above about 5% carbon dioxide is essential, a self-contained breathing apparatus should be used. Face masks for this apparatus should be issued on a personal basis and a register of use maintained by the fumigator-in-charge. Each time the mask is put on, its facial fit should be tested by closing the cylinder valve and inhaling deeply; the vacuum so created should cause the facepiece to adhere to the face for about 15 seconds. All air cylinders should be checked to ensure that they are fully charged. Partly filled cylinders *must not be used.*

D.3.3.2. Skin Protection

Carbon dioxide discharged as liquid from either bulk or cylinders is very cold, as is solid carbon dioxide (dry ice). Direct skin contact with either may lead to 'cold burns'. Pipes carrying newly vaporised gas can also be very cold and contact may also cause skin damage. Where hand contact with any of these sources of cold is likely, gloves should be worn.

D.3.4. Fumigation Personnel

D.3.4.1. Minimum Number of Persons

Fumigation with carbon dioxide is less hazardous than many other fumigation techniques because it is extremely unlikely that dangerous concentrations of carbon dioxide will build-up in unconfined work spaces. Because of this, there are circumstances where it would be safe for an unassisted person to carry out treatments, e.g. the dry ice treatment of shipping containers. However, *a minimum of two workers is recommended for all treatments.* This makes essential operations such as pressure testing, leak detection, and sealing much easier, and conforms

with the code of practice for other fumigants. For the fumigation of sheeted stacks, more persons may be needed to move and manipulate large fumigation sheets.

On the extremely rare occasions when self-contained breathing apparatus is used for access to areas with high carbon dioxide at least two persons should be present, one outside the danger area.

D.3.4.2. Qualifications of Personnel

The requirements of carbon dioxide fumigation both in terms of sealing standard and gas retention are rigorous. For a treatment to be successful, it is essential that the fumigator-in-charge understands the requirements of the technique, can carry out the tests needed to ensure that fumigation will be successful, and can also recognise a successful fumigation. This means that he will be able to carry out a simple pressure test and know how to carry out simple estimation of carbon dioxide concentration.

D.3.4.3. Monitoring of Health of Fumigation Staff

Where staff are part of a regular fumigation team, *the fumigator-in-charge should ensure that regular health checks are performed on himself and his staff.* This should be done in consultation with and according to the requirements of local health authorities.

D.3.5. Fumigation Practice

D.3.5.1. Formulations

D.3.5.1.1. Dry Ice

Dry ice is supplied as blocks, crushed ice, or pellets. These will usually be transported in some type of insulated container. Due to the low surface area to volume ratio in solid blocks, only a minimal amount of insulation is necessary. Crushed ice and pellets are best for initial gas addition due to their rapid volatilisation: blocks are useful to make up gas losses due to their slower gas release.

D.3.5.1.2. Standard Cylinders

Gaseous carbon dioxide is usually supplied by vaporising liquid carbon dioxide held under pressure in cylinders containing between 20 and 32 kg. As long as the temperature of the gas in cylinder remains above 15°C, and the pressure remains above 5000 kPa, a constant stream of gas can be obtained. If the temperature and/or pressure fall outside this range the liquid will solidify, and a much reduced gas flow will result.

D.3.5.1.3. Eductor Tube Cylinders

Eductor tube cylinders are designed to dispense liquid under pressure without the need to turn the cylinder upside down, and can conveniently be used for introducing carbon dioxide snow into fumigation enclosures. These cylinders, which normally contain 20–30 kg of carbon dioxide, are not usually available in large numbers.

D.3.5.1.4. Bulk

Bulk liquid carbon dioxide can be supplied in a large range of fixed and portable pressurised vessels, ranging in capacity from about 50 kg to many tonnes. The appropriate size of such vessels is best arrived at in discussion with the organisation supplying the gas. Such bulk vessels may be used to supply carbon dioxide as either snow or gas. The choice of which of these two to use will depend on the effects of localised temperature reduction on the enclosure fabric, which may become brittle and can break when frozen, and on the effects of localised cooling on the stored commodity.

D.3.5.1.5. Storage and Handling of Cylinders

Cylinders of carbon dioxide are under considerable pressure (approx. 7000 kPa at 30°C) and should be stored, handled, and used with care (see Appendix 7 for guidance on the safe storage and handling of gas cylinders).

D.3.5.3. Preparation for Fumigation

D.3.5.3.1. Planning

Before commencing a treatment, the fumigator-in-charge should prepare a plan describing the intended course of the fumigation. He should explain this plan in detail to persons involved in the fumigation, allocating responsibilities for particular aspects of the plan where appropriate. The plan should include how the fumigant is to be applied, how the enclosure is to be sealed, how the fumigant is to be vented after the treatment, at what times the various actions involved in the fumigation are to be carried out and who will carry them out.

D.3.5.3.2. Notice of intention to fumigate

The officer-in-charge of the premises to be fumigated must be advised by the fumigator-in-charge of the details of the treatment program and of the safety precautions to be observed. This advice should be tendered in the form of the notice shown in Appendix 2.

D.3.5.3.3. Sealing of Fumigation Enclosure

Sealing is an essential component of carbon dioxide fumigation. A readily sealable purge vent must also be fitted to the top of the storage enclosure, to permit escape of excess carbon dioxide during the application phase. Where it is intended to use only a single dose of carbon dioxide, it is essential that the enclosure meets a pressure decay standard on the fully loaded enclosure of a halving of differential pressure from approximately 250 Pa in longer than 5 minutes. Where a make up of gas is to be used, e.g. container fumigations, a different standard may be required. Details of

pressure testing are given in the other parts of these recommendations covering specific applications. If the enclosure fails the appropriate pressure test, it should not be used for carbon dioxide fumigation. If repeated attempts to seal are unsuccessful, the stack may need to be broken down and the floor sheet inspected.

It is important that all obvious leaks are sealed, even if the enclosure passed the pressure test. This is especially important where the sealed structure will also act as an insect-proof barrier to protect the commodity from reinfestation during the storage period.

D.3.5.3.4. Preparation for Ventilation of Fumigated Material

Depending on the size and nature of the sealed storage, it may be necessary to provide a means of post-fumigation ventilation for the enclosure. Where this is necessary, fans should be installed to allow fresh air to replace the headspace atmosphere. These fans need to be both sealable and controllable from the outside of the enclosure, and should be capable of several gas interchanges an hour. Where worker access to the enclosure is not likely (e.g. sealed bag stacks, bulk grain shipping containers), or where opening removes a considerable portion of the gas-proof barrier (shipping containers), no special requirements for ventilation are required.

D.3.5.3.5. Ventilation of Adjacent Areas

The only likely hazardous areas adjacent to a carbon dioxide fumigation are confined spaces surrounding the sealed enclosure and areas lower than the fumigation area, e.g. elevator boots, conveyor tunnels, basements, and under-floor spaces. Where access to these places cannot be restricted during fumigation adequate ventilation, either natural or forced, should be available.

D.3.5.3.6. Warning Signs

Where human access to a fumigation enclosure is possible each door should be locked and have a warning sign indicating that there is a potential risk of low oxygen or raised carbon dioxide, regardless of whether or not fumigation is actually in progress. It is important to remember that in a sealed enclosure there may be a build-up of carbon dioxide and a reduction of oxygen by natural processes such as respiration, especially in damp and moulding grain. Furthermore, in the post-fumigation period, grain which has been ventilated may nevertheless desorb significant quantities of carbon dioxide sorbed during fumigation.

The signs used should have a warning symbol appropriate to the country/culture concerned and should convey, in the local language(s), the information contained in the following English text:

WARNING
SEALED STORAGE
This structure may contain
toxic levels of carbon dioxide or low levels of oxygen
CHECK BEFORE ENTERING

During actual fumigation and any post-fumigation, unventilated storage period, there should be affixed to each door and other means of access to the fumigation area, a notice with a white background on which is printed, in the local language(s), the words:

DANGER—KEEP OUT
POISON GAS
FUMIGATION WITH CARBON DIOXIDE

in capital letters not less than 10 cm (3 inches) high, in a colour contrasting with the background. These signs should also incorporate a warning symbol appropriate to the country/culture concerned.

The authorised fumigator's name, contact address, and telephone number must be clearly shown at the foot of the notice, together with the date of commencement of fumigation. The form of notice suggested is shown in Appendix 3.

Where there are unventilated confined areas around the fumigated enclosure, or confined spaces lower than the stack, a notice warning of the potential accumulation of carbon dioxide should be displayed. These signs should have a warning symbol appropriate to the country/culture concerned and should convey, in the local language(s), the information contained in the following English text:

WARNING.
This area may contain
toxic levels of carbon dioxide
CHECK BEFORE ENTERING

All warning notices should be suitably illuminated at night.

D.3.5.3.7. Final Safety Checks

Before finally sealing any fumigation enclosure, especially those with easy worker access, all accessible places within the enclosure must be inspected by the fumigator-in-charge to ensure that all personnel have left the enclosure. Immediately after the inspection, the fumigator in charge will ensure all access points are closed, locked, and fumigation warning notices are in place. He will also ensure the purge vent is open and can safely be closed.

If the fumigation is in an unventilated confined area, all other workers in the area must leave, especially during the gas introduction phase. In a well ventilated area, workers should not work at floor-level within 2 m of the structure during gas addition.

D.3.5.4. Application of Formulations

D.3.5.4.1. Bag Stacks

Carbon dioxide is added to bag-stacks as 'snow' or vaporised gas obtained from

cylinders or bulk. The snow should be introduced to the base of the stack and not in direct contact with the bags of commodity. This many be achieved by discharging the snow below the timber dunnage forming the base of the stack or, if dunnage is absent, by building the stack with a small tunnel at its base.

D.3.5.4.2. Bulk Grain

Where large bulks of grain are to be treated, it is essential that the carbon dioxide entering the grain is at a temperature close to that of the grain. This is achieved by vaporising liquid carbon dioxide and heating the gas before it enters the grain, thus avoiding any risk of condensation on the grain. For small bulks of grain, it may be possible to apply snow into aeration ducting without causing condensation problems.

D.3.5.4.3. Empty Structures

Empty structures may be fumigated with carbon dioxide using application and sealing methods as detailed in the other parts of the recommendations covering specific types of fumigations.

D.3.5.5. Dosage Rate and Exposure Periods

The aim with a carbon dioxide fumigation is to expose any insects present to a concentration of carbon dioxide above 35% for longer than 15 days. The dosage applied to achieve this will depend on:

- the initial concentration achieved
- the leakage rate of the enclosure
- the displacement volume of the commodity
- the amount sorbed by the commodity
- the efficiency of purging.

As these factors will vary vastly between enclosures, a set dosage per tonne of commodity can be only a rough guide to the required dosage. A more economic and reliable approach is to observe the concentration within the enclosure and to stop adding gas when the average concentration (or the concentration at the top of the enclosure) reaches 75% carbon dioxide. In a correctly sealed enclosure, this will give a concentration of greater than 35% at 15 days after treatment.

In a sealed enclosure meeting the pressure test standard, a concentration of greater than 75% carbon dioxide should require no more than 1.7 kg of carbon dioxide per cubic metre of total storage space. The amount less than 1.7 kg/m^3 will depend on the actual values attributed to 1–5 above. In a full storage with effectively zero head-space, the dose rate to achieve greater than 75% has been observed to be about 1.2 kg of carbon dioxide per tonne.

D.3.5.6. Fumigation Records

A record of the fumigation must be kept. Ideally, at least two copies are needed, one kept attached to the outside of the fumigation sheet, the other in a fumigation log book. This record should show:

- the location of the treatment
- type and tonnage of commodity treated
- type of storage—bag, bulk, container
- volume of enclosure*
- time when pressure decay (gastightness) test was done and results of test*
- date treated with carbon dioxide*
- carbon dioxide concentration near the top of the enclosure 2 days after treatment*
- carbon dioxide concentration near the top 15 days after treatment*
- date the stack was opened and/or ventilated*
- time of issue of declaration of clearance*
- details of any incidents or accidents.

Items marked with an asterisk should also be recorded on stack/bin cards.

These records are designed to aid in the management of the stocks and, in particular, to use sealed storage to its maximum advantage. Should the target of greater than 35% carbon dioxide for longer than 15 days not be achieved, the commodity should not be stored for a long period in the sealed enclosure as there is a possibility that a complete disinfestation has not been achieved and pest-induced moisture migration may occur.

D.3.5.7. Clearing the Fumigant

D.3.5.7.1. Ventilation of the Commodity and Enclosure

If ventilation is needed to gain access to the enclosure, it should be continued until the headspace concentration is less than 0.5% carbon dioxide. Sorbed gas will continue to be given off from the commodity for some time. The carbon dioxide concentration inside the enclosure must be measured again if the enclosure was closed after ventilation was stopped.

D.3.5.7.2. Testing Fumigant Clearance

Before clearing the storage for worker access, and before moving grain through sub-floor spaces, it is essential to ensure that carbon dioxide concentrations are below 0.5%. This should be done by taking gas samples from the headspace near the grain surface and from within the lower levels of the grain.

D.3.5.7.3. Post-Treatment Action

A correctly sealed enclosure, appropriately treated with carbon dioxide, will remain free of and protected from insects as long as it remains sealed. If the enclosure is to be used for long-term sealed storage, it is essential that good hygiene be practiced around the enclosure, that a rodent control program is carried out, and that the enclosure is inspected for damage on a regular basis during the storage.

D.3.6. First Aid

A person who appears to have been affected by carbon dioxide must be taken at once into fresh air, kept quiet and warm, and medical attention should be obtained. If breathing stops or shows signs of failing, resuscitation must be commenced immediately.

Cold burns or frost bite caused by skin contact with solid carbon dioxide (dry ice) should be flushed with lukewarm water for at least 5 minutes, then treated as if they were heat burns. Hospital attention should be sought for all but the most superficial cases. Do not apply direct heat or give alcohol or cigarettes. Protect frozen parts from infection.

D.3.7. Witholding Period

Treated commodities are safe for human consumption or for stock feed, and may be safely transported, immediately following completion of the recommended ventilation period.

D.4. Hydrogen Cyanide

D.4.1. Objectives and General Requirements

The following code is designed to provide details of the principles underlying effective fumigation with hydrogen cyanide. These principles cover both safety and efficacy.

Hydrogen cyanide fumigations are carried out to eradicate pests, particularly rodents, from commodities, storage enclosures and transport. They are useful where commodities are dry, a short exposure is required and methyl bromide is unsuitable. Treatment of seeds required for sowing is an important potential use.

Hydrogen cyanide is in very limited use at present, because of its inconvenient properties and its justified reputation for toxicity to man. *Its application should be considered only where the other common fumigants are inappropriate.*

A well sealed enclosure around the commodity is essential to retain the gas for sufficient time for the fumigant to be distributed and act on the pests, and also to prevent a health hazard to humans and valuable animals outside the enclosure. Hydrogen cyanide can be introduced as gas or generated within the enclosure. It can also be supplied impregnated on cardboard disks. Forced distribution of hydrogen cyanide is always required so that an even distribution of gas can be achieved rapidly. At the end of the exposure period, (typically 24 hours for insect control, 2 hours for rodent control), the gas must be removed by forced ventilation to a level where it poses no health hazard.

Hydrogen cyanide seldom produces adverse effects on commodities. However, if no information is available on the particular application, it should be tested on a small scale before extensive use. Deleterious effects are particularly likely on high moisture content commodities. Hydrogen cyanide reacts reversibly with sugars and dissolves in water. Commodities with high sugar and water contents may thus contain high cyanide residues after treatment. Complete removal of these residues by aeration may be slow. However, the permitted residue is high: 75 ppm for cereal grains. Cyanide is a common natural component of foods, including some cereal grains.

D.4.2. Hydrogen Cyanide as a Fumigant

D.4.2.1. General Characteristics and Warning Properties

Under tropical conditions (> 26°C) hydrogen cyanide is colourless gas with a strong odour of bitter almonds to most, but not all, people. It is easily liquefied under pressure. Because of its high boiling point it tends to remain in the liquid state when released under pressure into a commodity or enclosure, unless precautions are taken to prevent this. Hydrogen cyanide is flammable in air over a substantial range (6–46%) and hydrogen cyanide/air mixtures within this range may explode violently.

Hydrogen cyanide may be supplied as a liquid under pressure in cylinders,

When and when not to use hydrogen cyanide as a fumigant

Hydrogen cyanide is the fumigant of choice for:

- vertebrate pest control in enclosures, such as buildings or ships
- where a rapid treatment is required and germination must be preserved
- where a rapid treatment is required and the equilibrium relative humidity of the commodity is less than 60% and methyl bromide may lead to taint or excessive residues.

Hydrogen cyanide should not be used:

- where there is a risk of leakage into work spaces or habitations
- where there are no properly trained, qualified, and protected fumigation staff
- where there are moist commodities or free water within the fumigation enclosure
- at ambient or commodity temperatures lower than 26°C.

absorbed into cardboard disks, or it may be generated within the fumigation enclosure by the action of moisture on calcium cyanide.

The basic properties of hydrogen cyanide are as follows:

chemical formula	HCN
molecular weight	27
boiling point (°C)	25.7
specific volume at 30°C, 1 atm (m^3/kg)	0.904
specific gravity (gas) [air = 1.0]	0.95
gas density at 30°C, 1 atm (kg/m^3)	1.107
vapour pressure at 30°C (atm)	1.20
conversion factor, g/m^3 to ppm (30°C, 1 atm)	890
flammability limits in air (%, v/v)	6-46
solubility in water	miscible
specific gravity at 30°C (liquid, kg/L)	0.688

Hydrogen cyanide reacts chemically with aldehydes and ketones (organic compounds) in commodities. In the presence of water it acts as a mild acid. Liquid hydrogen cyanide is a powerful solvent for organic compounds, removing plasticisers from materials such as PVC and dissolving many materials, e.g. many plastics and rubbers.

Liquid hydrogen cyanide is prone to polymerisation (individual molecules combine to form long, chain-like molecules), in some situations violently. The reaction is

Effects of hydrogen cyanide exposure on humans

HCN concentration (ppm)	*Effect*
10	Threshold Limit Value — Ceiling: not to be exceeded during any part of the working exposure
25	Slight symptoms after several hours of exposure. May lead to chronic poisoning.
50	Serious disturbances after 0.5–1 hours exposure.
100	Dangerous — possibly fatal — after 0.5–1 hours exposure.
200	Quickly kills humans

catalysed by alkalis. Liquid hydrogen cyanide supplied in cylinders will slowly polymerise. Consequently, hydrogen cyanide cylinders must be used within a short time after receipt. As supplied, the liquid is stabilised by adding a small quantity of acid (e.g. 0.05% sulphuric acid).

D.4.2.2. Adverse Effects on People

Hydrogen cyanide is extremely toxic to humans, affecting cytochrome oxidase, a crucial enzyme involved in respiration. The effect of exposure to high concentration is very rapid, quickly leading to severe breathing difficulties and unconsciousness and, unless treated, to death. Mild poisoning symptoms include general weakness of the limbs, breathing difficulties, headache, giddiness and vomiting.

Hydrogen cyanide may be absorbed both by inhalation and through the skin.

The specific antidote for cyanide poisoning is cobalt edetate (Kelocyanor) injections. Note, however, there must be a positive diagnosis that cyanide poisoning has occurred before this antidote is used as otherwise it can produce adverse effects itself. With prompt treatment, persons overexposed to cyanide usually recover completely. Note too that although onset of symptoms may be rapid, an affected person may live for several hours and it may still be possible to bring about recovery, given remedial treatment.

D.4.2.3. Adverse Effects on Commodities

Hydrogen cyanide when used on low moisture commodities has little adverse effect either on germination or end use properties. The main limitation is concerned with formation of excessive residues.

Hydrogen cyanide reacts with reactive carbonyl groups in commodities to make cyanhydrins: this reaction is reversible. Because of its high boiling point and solubility in water, hydrogen cyanide is also sorbed physically to a substantial extent on commodities through capillary condensation and dissolution. This process is also reversible. Residue tolerances are expressed in terms of cyanide content (75 ppm in raw cereals, 7.5 ppm in flour). Aeration quickly removes much of the sorbed cyanide. However, a proportion that is more strongly held, probably in some chemical compounds, is released only slowly.

D.4.2.4. Detection and Measurement

The apparatus used depends on the situation and concentration to be measured.

Insecticidal concentrations (up to about 30 g/m^3). Hydrogen cyanide concentrations at pesticidal levels can be measured by detector tubes (e.g. Dräger, Auer, etc.) or by thermal conductivity meter (e.g. Fumiscope) calibrated for hydrogen cyanide.

Health limit concentrations (0.01 g/m^3, 10 ppm approximately). Concentrations in the range of the TLV can be measured by detector tube (e.g. Dräger, Auer).

Residues. The residual HCN in foodstuffs is transferred by steam distillation into an absorbing solution containing sodium sulphide or sodium bicarbonate. The cyanide can then be estimated colorimetrically in the absorbing solution. A number of standard techniques are available.

D.4.2.5. Warning Agents

Approximately 60% of humans can detect low levels of hydrogen cyanide — minimum 2–5 ppm in air — by smell. These levels are below the hygienic standard. Leakage of hydrogen cyanide from cylinders and tins can be detected using moistened methyl orange papers. Chloropicrin, a potent lachrymal agent, is usually added to tins of HCN-impregnated cardboard disks to act as a warning agent.

D.4.3. Personal Protection

D.4.3.1. Respiratory Protection

Fumigators and other persons at risk from inhaling excessive quantities of hydrogen cyanide must be provided with either a full-face canister respirator or an open-circuit, self-contained breathing apparatus with full face mask. Respiratory protection must be worn whenever there is a danger that the local atmospheric HCN concentration will exceed the hygienic standard of 10 ppm.

Masks and canisters should be issued on a personal basis and a register of use maintained by the fumigator-in-charge.

D.4.3.1.1 Canister Respirators

Canister respirators should be fitted with a canister designed for protection against hydrogen cyanide, as recommended by occupational health authorities. Each time a respirator of this type is worn, the facial fit should be tested by closing the inlet to the canister with the palm of the hand and inhaling deeply; the vacuum so created should cause the facepiece to adhere to the face for about 15 seconds.

With this type of respirator it is essential that the canister be used within its stated shelf life. The respirator canister must always be replaced before either its shelf life has expired or when the recommended usage time has been reached. Note that the life of canisters is considerably reduced when they are used in humid situations. The expiry date of a canister may easily be calculated since each is marked with the date of manufacture and shelf life.

Canisters should be stored in a sealed condition in a cool, dry, well-ventilated place away from contamination by any fumigants. The following precautions should always be observed:

- Canisters may be used to provide protection against only low concentrations of hydrogen cyanide—not more than 1% by volume—and are effective for only a limited time.
- Record the date when the canister is attached to the respirator facepiece after the top seal is removed. This is best done by writing the date on a small adhesive label which must be affixed to the canister. This label can be used as a 'log' to record exposure of the canister to the the fumigant.
- Before using the respirator, remove the cap and the seal over the air inlet valve of the canister. Again, at this time mark the date on the 'log' label. Always replace the seals after use. The canister must be replaced 3 months from the first time of use, even if there has been no known exposure to fumigant.
- After any fumigation in which there has been prolonged exposure to low concentrations of the fumigant or accidental exposure to high concentrations, immediately discard the canister. As a guide, 1 hour of wearing is the usual period after which a canister should be discarded. Canisters should be replaced after two or three usages. Allow a wide margin of safety in estimating exposure times because under conditions of high ambient humidity canisters become ineffective rapidly. This can be made worse where respirator and canister valves are faulty so exhalation may occur partially through the canister. If there is any doubt about the exposure life of a canister, *discard it,* as canisters cost little in terms of health of the individual.
- Canisters should be resealed with the original top and bottom seals between uses.
- Discarded canisters should be rendered unusable by crushing the inlet port and then disposed of under conditions which will prevent them from being picked up and used again for any purpose.
- Canisters that show any sign of external damage should be considered worthless, and must be discarded. A severe blow on the metal covering may cause displacement of the contents, permitting contaminated air to pass through to the wearer.

- Immersion of the canister in water renders it useless. Water can enter the canister through the facepiece. Disconnect the hose and canister before cleaning or disinfecting the facepiece.

D.4.3.1.2. Self-contained Breathing Apparatus

Self-contained breathing apparatus is the preferred form of respiratory protection for hydrogen cyanide fumigations whenever this equipment is available. *It is the only type of respiratory protection to be used in emergencies where fumigators have succumbed to the gas. Thus, at least one set must always be on hand when HCN treatments are being carried out.*

The facial fit of this type of apparatus is tested in a manner similar to that employed with the canister respirator, except that the cylinder valve is closed prior to deep inhalation. Before using any self-contained breathing apparatus, it is essential to ensure—by inspecting the pressure gauge—that the cylinder is fully charged with compressed air.

D.4.3.2. Skin Protection

A cotton boiler suit (coverall or overall), with full arms and buttoned at the throat, should be worn by all persons engaged in hydrogen cyanide fumigation. Impervious gloves and footwear should also be worn. Note that this clothing provides no protection against absorption of hydrogen cyanide through the skin (see Section 4.2.2.). Any protective clothing contaminated by liquid hydrogen cyanide or calcium cyanide must be removed immediately after evacuation to a safe, well ventilated place.

Any person who has had skin contact with hydrogen cyanide liquid or vapour should have the affected area washed by flooding it with water from a shower, fire hose, etc. Remove wet clothing, gloves, shoes and socks. Wash skin thoroughly with copious amounts of water, keep the victim warm and apply first aid. Thereafter, all contaminated clothing should be thoroughly decontaminated by first deluging it with water and drying it. It must then be laundered before being worn again.

D.4.4. Fumigation Personnel

D.4.4.1. Minimum Number of Persons

Treatment of permanent enclosures of up to 10 000 m^3 capacity should be performed by a team including *no fewer than three (3)* qualified and experienced fumigators. One of these people should always be designated as the fumigator-in-charge (see next section). An additional person is required for each additional 5000 m^3 of volume to be fumigated. All such personnel must be provided with a personal self-contained breathing apparatus. It shall be their duty to ensure that:

- the cylinders are refilled with air immediately after every usage; and
- the apparatus is properly functional.

One person, selected by the fumigator-in-charge, will be responsible for monitoring fumigant concentrations and will be in the workplace at all times to ensure that approved hygienic limits are not exceeded.

Treatment of bag-stacked commodities under removable fumigation sheets shall be performed by a team including *no fewer than two (2)* qualified and experienced fumigators. One of these should always be designated the fumigator-in-charge.

D.4.4.2. Qualifications of Personnel

At least one member of the work force employed in each fumigation should be designated fumigator-in-charge and be given responsibility for the safe and effective execution of the work.

The fumigator-in-charge must hold (where applicable) a licence to fumigate with hydrogen cyanide. He should have a minimum of two years active involvement in the fumigation of structures and/or stored products with hydrogen cyanide and a detailed knowledge of fumigation practice. He must be able to recognise the symptoms of hydrogen cyanide poisoning and be fully trained and able to apply the specific first aid measures required to treat this condition. He must be present at all times during the active phases of each fumigation under his control. In addition to the organisation and supervision of the work of his subordinates, his duties should include:

- the planning of the fumigation and the procurement of materials and equipment;
- the thorough instruction of his subordinates with respect to safety precautions, the maintenance and correct use of protective equipment, first aid, the general work plan, and individual tasks;
- ensuring the performance of tests for the fumigant gas and the issue of clearance certificates;
- provision of a fully equipped first aid kit whose contents are not time expired; and
- the location of the nearest medical practitioner or medical facility to be informed when a hydrogen cyanide fumigation is to be undertaken.

The other fumigators in the gang should hold a fumigation licence and have some experience in the general practice of fumigation. Persons without fumigation experience may be employed as fumigators' assistants provided that they are trained in advance of treatment, with emphasis on the properties and hazards of hydrogen cyanide, fumigation procedure, the use and maintenance of required protective equipment, and the specific first aid measures required for this fumigant.

D.4.4.3 Monitoring Health of Operators

Where staff are part of a regular fumigation team, the fumigator-in-charge should ensure that regular health checks are performed on all members of the team to

ensure they are fit to undertake this work. This should be done in consultation with and according to the requirements of local health authorities.

D.4.5. Fumigation Practice

D.4.5.1. Formulation

Hydrogen cyanide is available as a liquid in steel cylinders. It should contain a stabiliser to extend its storage life. Even if it does, however, storage life is usually limited to six months, after which the liquid tends to become explosive. This hazard is hastened when cylinders are stored in sunlight and become hot.

Hydrogen cyanide gas may be released from cardboard disks impregnated with liquid hydrogen cyanide. These are sealed in tins and may also contain chloropicrin as a lachrymal warning agent. Such tins must be opened with care, as the contents are under positive pressure.

Hydrogen cyanide can also be generated for fumigation purposes from calcium cyanide powder, which is supplied packed in tins. When admixed with grain, this reacts with atmospheric moisture to release hydrogen cyanide gas.

D.4.5.2. Storage and Handling of Formulations

Liquid hydrogen cyanide has a limited storage life of six months, after which it must be returned to the manufacturer. It is important, therefore, not to overstock this fumigant. The date of manufacture and receipt should be prominently marked on the cylinder.

Under no circumstances should cylinders of hydrogen cyanide, whether full or empty, be stored so that they are exposed to the sun. Heating hastens polymerisation of liquid hydrogen cyanide which causes it to become explosive. It is advisable to monitor the pressure within such cylinders. This should be done and recorded when they are first received and again immediately before they are used. Any large increase in pressure may be indicative of polymerisation.

Hydrogen cyanide stocks and those of the chemicals from which it is generated should be stored in cool, shaded, dry, well ventilated and secure/lockable enclosures. The keys of such stores should be held by a designated person, responsible for its safekeeping and the conduct of the store. The store must carry a warning sign on the door signifying presence of poison gas or chemicals. Access should be restricted to nominated and responsible staff *equipped with respiratory protection.*

Cylinders of liquid hydrogen cyanide must be used on a first in, first out basis and precautions must be taken to ensure that no cylinder is held for longer than six months. Cans containing impregnated cardboard disks or calcium cyanide can become rusty and unsafe if stored poorly. Stocks should be inspected regularly—preferably at monthly intervals.

All cylinders, cans and chemicals used for generating hydrogen cyanide should be transported only in well ventilated cargo areas outside the passenger compartments of vehicles. Respiratory and first aid equipment must be available to persons involved in transport of hydrogen cyanide or chemicals used to generate it. They should be trained in its use and be aware of the hazards of hydrogen cyanide in case of an accident.

Precautions

- Cyanides must be stored in labelled closed containers in a place accessible only to authorised persons.
- Gloves must always be worn when handling cyanides.
- Hands and face must be washed before eating, drinking or smoking after handling cyanides.
- Food, drink and utensils must not be brought into places where cyanide is present. These areas shall be designated as no-smoking, no-eating areas.
- Any contaminated clothing should be removed and laundered safely. Under no circumstances should contaminated clothing be taken home (see **Section D.4.3.2**).
- Always keep calcium cyanide apart from acid, because HCN gas is rapidly released on contact with acid.

D.4.5.3. Preparation for Fumigation

D.4.5.3.1. Planning

Before commencing a treatment, the fumigator-in-charge should prepare a plan describing the intended course of the fumigation. He should explain this plan in detail to all persons involved in the fumigation, allocating responsibilities for particular aspects of the plan where appropriate. The plan should include how the fumigant is to be applied, how the enclosure is to be sealed, how the fumigant is to be vented after treatment, at what times the various actions involved in the fumigation are to be carried out and who will carry them out. Since forced mixing will be required, the required fans and duct work must be in place. Any piping used to convey the fumigant to the enclosure must be designed so that no liquid hydrogen cyanide comes into direct contact either with foodstuffs or other commodities and must be made of material not affected by this fumigant.

D.4.5.3.2. Notice of Intention to Fumigate

An authorised fumigator intending to fumigate a building or other enclosed space shall deliver a notice in writing 24 hours prior to the fumigation commencing in the form of Schedule No. 1 (see Appendix 2) to:

- the appropriate authority;
- the nearest Police Station and Fire Brigade;
- the nearest medical practitioner or medical facility; and
- every tenant or occupier within the fumigation and risk area who must acknowledge receipt by signing the duplicate copy which shall be retained by the fumigator.

D.4.5.3.3 Definition of Risk Area

There is a risk area around a fumigation enclosure comprising all adjacent spaces in which harmful concentrations of hydrogen cyanide might, in the opinion of the fumigator-in-charge, become present. The risk area may be entered only by permission of the fumigator-in-charge. It should be conspicuously marked to warn people not involved in the fumigation operation to stay out the area. Warning notices must display the identity of the fumigant and the name and address of the fumigator-in-charge, together with emergency telephone numbers. Special care should be taken over buildings or rooms with walls common to an area that is to be fumigated which must be evacuated for the duration of the treatment. Where necessary, the fumigator-in-charge should take possession of any keys to doors in the fumigation and risk area.

In open spaces the risk area is defined as that within 6 m of the edge of the fumigation enclosure.

D.4.5.3.4. Sealing the Fumigation Enclosure

The enclosure in which the fumigation is to be conducted must be made as gastight as practicable. Methods of sealing and testing for gastightness are given in Appendix 5 and, in more detail, in the other parts of these recommendations covering operational procedures for specific applications. Any fumigation using forced recirculation or carried out within 30 m of a work space or habitation and involving more than 2 kg of hydrogen cyanide shall be carried out in an enclosure meeting a pressure test where a pressure halving occurs in not less than 5 minutes.

Fumigation sheets, where used, must be intact, free from holes and tears. They must be joined by the roll and clamp system. Such sheets must be adequately 'sealed' to the floor of the storage so that gas loss is reduced to the absolute minimum for this form of fumigation. The use of loose sand for this purpose is preferred to 'sand snakes'.

D.4.5.3.5. Ventilation of Adjacent Areas

Preparation for the ventilation of areas adjacent to the treatment enclosure must be made before introduction of the fumigant. Enclosed areas adjacent to a fumigation enclosure must be subject to forced ventilation at not less than 1 air change per hour throughout the treatment until the fumigation area is declared free of gas. Open areas adjacent to a fumigation and under natural ventilation should be entered only by personnel with respiratory protection and then only after the atmosphere has been tested for hydrogen cyanide.

There should be good ventilation, artificial if necessary, at the point from which the operators apply the fumigant.

D.4.5.3.6. Warning Signs and Precautions to Prevent Entry

The fumigator-in-charge of the fumigation of any building, vessel, or enclosed space shall, immediately before the application of fumigant, affix to each door and other means of access to the fumigation area, a notice with a white background on which there shall be printed, in the local language(s), the following English text:

DANGER–KEEP OUT
POISON GAS
FUMIGATION WITH HYDROGEN CYANIDE

in capital letters not less than 10 cm (3 inches) high, in a contrasting colour to the background. A symbol denoting deadly danger, equivalent to the 'skull-and-crossbones' used in many western countries, could also be incorporated in the sign.

The authorised fumigator's name, contact address, and telephone number must be clearly shown at the foot of the notice. The form of notice suggested is shown in Appendix 3.

All warning notices must be suitably illuminated at night.

If possible, preparation must be made to lock or bar all access points to the risk area. Two watchmen should be present at the start of the fumigation and should remain on site well outside the risk area, throughout the treatment, to ensure unauthorised and unprotected persons do not enter the risk area.

D.4.5.3.7. Final Safety Checks

No person shall commence to fumigate any building or other enclosed space until:

- The fumigator-in-charge has personally checked all portions of the fumigation area and risk area to ensure that no persons or domestic animals remain therein.
- All fires and naked lights within the fumigation area have been extinguished and all oil, gas and electricity supplies have been turned off at the mains. They must remain off until the clearance certificate has been issued.
- All liquids and foods which are liable to absorb the fumigant have been removed from the fumigation area.
- All sources of water are turned off at the mains and, where possible, all reservoirs within the enclosure have been emptied.

- All windows and ventilators in the risk area have been opened to provide maximum ventilation.
- Fans, as required, are in position and tested for efficiency.
- The nearest operable telephone has been located and its number noted.
- It has been confirmed with Police and Fire Stations that fumigation is about to commence.
- It has been confirmed with the nearest medical practitioner or medical facility that fumigation is about to commence.

D.4.5.4. Fumigant Application and the Holding Period

D.4.5.4.1. Liquid Hydrogen Cyanide

Liquid hydrogen should be vaporised before introduction into the enclosure through suitable pipework. Introduction is effected by pressurising cylinders with compressed nitrogen or air to drive the liquid through the eductor (siphon) tube out of the cylinder and through the vaporiser. *It is important to ensure that no liquid hydrogen cyanide remains trapped between valves at the end of this operation.* Rubber gloves should always be worn when working with hydrogen cyanide-containing cylinders or pipes.

All application equipment must be leak-free. The fumigators must wear protective clothing and respiratory protection during the application of the fumigant. Operators must wear respiratory protective equipment at all times while they are within the risk area.

Methyl orange papers or hydrogen cyanide specific detector tubes should be used to detect leakages in the application equipment and piping outside the fumigation area, especially at joints and couplings. Any leakages must be corrected by two operators wearing adequate self-contained breathing apparatus and suitable protective clothing before continuing with the fumigation.

In the event of an emergency (for example, if a delivery pipe becomes broken or disconnected and leakage of fumigant is possible) two fumigators wearing self-contained breathing apparatus should close the main cylinder valve and then withdraw from the risk area. A third fumigator, similarly equipped, should be on standby observing the first two fumigators ready to render assistance. All other fumigators should withdraw at once. *The observer must not give any assistance before contacting the nearest doctor or medical facility and notifying other fumigators.*

In circumstances where it is considered to be too hazardous for any remedial action to be taken, the fumigation should be abandoned, all fumigators should withdraw immediately and the appropriate authorities notified. It will, in such cases, be necessary to extend the risk area and exclude all personnel.

After a period of ventilation, two fumigators should check the concentration in the risk area whilst continuing to wear respiratory protective equipment. When the concentration is below the short-term exposure limit they may then carry out the necessary adjustments or repairs.

After application of the fumigant, the enclosure should be checked for leaks using methyl orange papers or detector tubes. Leaks down wind may be detected readily, but those up wind may not be evident as they will not be passing hydrogen cyanide gas. These must be checked and, if necessary, sealed when the wind has dropped. All leaks found should be remedied before the fumigation team leaves the site. Respiratory protection must be worn during this procedure.

When applied for insect control, hydrogen cyanide concentrations in the fumigation enclosure should be monitored at not less than 6-hourly intervals during the holding period, using gas sampling lines fitted before application of the fumigant.

D.4.5.4.2. Calcium cyanide—application to bulk grain.

Calcium cyanide fumigant is fed into the grain stream at rates relative to the rate of grain flow according to the dosage required. The amount of gaseous hydrogen cyanide yielded is between 25-50% of the given weight of the granular material.

Grain so treated should remain under fumigation for at least 72 hours to allow for complete evolution and distribution of the fumigant. This period will be lengthened according to dosage, but 120 hours is sufficient for any dosage rate.

D.4.5.4.3. Impregnated Disks

Hydrogen cyanide may be absorbed onto cardboard disks. These are packed in tins that can withstand the pressure exerted by the gas. Because of the internal pressure, care must be exercised when opening such tins. It is advisable to precool them to below 10°C before they are opened. This can be done in ice cold water, or ice.

Protective clothing, including rubber gloves and respiratory protection, must be worn when opening these tins and the special opener supplied by the manufacturers must be used. Care must be taken to ensure that they are opened in such a way that any escaping gas is directed away from the fumigators. In addition, it is advisable for the fumigators, during this operation, to wear the canisters of their respirators on the back of the body, at the end of a longer hose, rather than in front.

The disks are distributed in the enclosure according to the required dosage. Rubber gloves and respiratory protection must be worn during this operation.

D.4.5.4.4. Dosage Rates

Table D3 gives typical dosage rates for HCN for various situations. The exposure time for treatment of empty stores against residual insect infestation may be

Table D3. Dosage rates for hydrogen cyanide treatment of grain and empty stores.

Situation	Dosage	Exposure Period
Empty warehouses, ships and barges, for control of residual insects	8 g/m^3	24 hours, with forced circulation
Empty warehouses, ships and barges for control of rodents	2 g/m^3	2 hours, with good distribution
Bulk grain with liquid HCN from cylinders, for insect control	50 g/t	24 hours, with recirculation
Bulk grain with calcium cyanide, as $Ca(CN)_2$, for insect control	80 g/t	5 days
Bagged grain under gas-proof for insect sheets, for insect control	50 g/t	24 hours, with forced distribution

shortened to 12 hours, provided all accumulations of grain residues have been cleaned away before treatment.

D.4.5.4.5. Clearing the Fumigant

At the completion of the fumigation period, the fumigation enclosure and risk areas must be ventilated. As hydrogen cyanide may be extensively sorbed, respiratory protection should be worn by all persons involved until hydrogen cyanide can no longer be detected at above the hygienic standard in the free atmosphere around the treated commodity.

The sequence and speed of the clearing operation should be decided by the fumigator-in-charge after considering factors such as the concentration of fumigant within the enclosure, the volume of the storage, wind velocity and direction, and the proximity of inhabited buildings. With large fumigations under sheets, the opening of the seams and removal of sheets should be gradual, with alternate periods of work and ventilation, until concentrations in the stack are low enough to permit safe removal of all sheets. There should be maximum ventilation of the working area, using dispersal fans where possible.

If HCN impregnated disks have been used, the spent disks must be collected after airing is complete and disposed of by burial in a secure site. The atmosphere in the risk area and fumigation enclosure should be tested periodically by the fumigator-in-charge until the hydrogen cyanide concentration has fallen below the hygienic limit. Special account should be taken of sorbent materials which may desorb gas for some time after the conclusion of the operations. All water reservoirs e.g. toilet bowls, basins etc. within the enclosure, that had not been emptied prior to treatment, should be flushed at least twice.

The fumigator-in-charge should then issue a certificate of clearance (see Appendix 4) when satisfied that the areas are safe for reoccupation. Warning notices should be removed or effectively defaced and barriers removed. Civil authorities notified that the fumigation was to take place, should be informed of its completion.

Vaporisers, piping, and other apparatus associated with the fumigation should be blown out mechanically with compressed air in a well ventilated safe place, before being stored or transported. All cylinders and piping should be checked to ensure that no gas remains trapped between valves. All fumigation sheets should be aired for not less than two hours before rolling for storage and future use.

D.4.5.4.6. Record Keeping, Including Assessment of Effectiveness of Fumigation

The fumigator-in-charge must maintain a written record of each fumigation carried out. The record must include:

- the names of all personnel engaged either on grain handling or fumigation work during the application of the fumigant, and the nature of their duties
- the location of the treatment
- type and tonnage of commodity treated
- volume of enclosure*
- results of gastightness test*
- date and time of commencement of fumigant application*
- the dosage applied and exposure time*
- Ct product achieved*
- length of airing period*
- time of issue of declaration of clearance*
- when sampling lines were installed, details of all measurements of concentrations obtained from within the fumigation enclosure*
- details of any incidents or accidents.

Items marked with an asterisk should also be recorded on stack/bin cards.

Copies should be kept of all notices issued and of clearance certificates. A register of issue and use of protective equipment should be kept.

D.4.6. First Aid

D.4.6.1. Entering Contaminated Area

If a person becomes incapacitated in a fumigation enclosure or risk area, rescuers entering must be adequately protected with self-contained breathing apparatus. *Canister type respirators cannot be used under these circumstances.*

D.4.6.2. Evacuation of Succumbed Person

Carry the patient to the fresh air and lie him or her down.

In the case of an accident, one person should begin first aid treatment while another calls a doctor and ambulance, giving details of gas and circumstances of exposure.

Measures to be taken while awaiting arrival of medical aid:

- apply artificial respiration and cardiac massage if required
- loosen all tight clothing
- remove contaminated clothing, including wrist watch and spectacles
- for skin contamination, thoroughly wash affected area with clean water
- for eye contamination
  - hold eyelids open and wash eyes immediately with a gentle flow of water
  - continue washing until doctor arrives
  - do not use any chemicals, they may increase the injury.

D.4.7. Withholding Period

Allow a period of 2 days after completion of ventilation before using treated commodities for human consumption or for stock feed.

Treated commodities may be safely transported after completion of the recommended ventilation period.

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Appendices

Appendix 1

Methods of Detecting and Measuring Resistance to Fumigants

Preamble

The method reprinted in the following 14 pages has been extensively used since it was developed and first published in 1975. It is still the most effective way in which resistance to either methyl bromide or phosphine can be detected.

Based on experience in use of the method during the years since its publication, a number of points can be made.

1. It is important to adhere to the use of three doses for each test, i.e., one at the discriminating dosage and the other two above and below the discriminating dosage. This procedure, in conjunction with the use of reference strains whose response is known, is designed to detect overdosing as well as underdosing.

2. Care should be taken to ensure that the source of methyl bromide is pure, as indicated by its colour. 'Pure' methyl bromide is water white while 'impure' material is typically straw yellow.

3. Because of possible variation in the speed of action of fumigant in different strains, at least two observations of mortality should be made. The first should be in accordance with the Test Method at 14 days, while the second should be a week later. If no more than the odd insect dies between the first and second observations it may be construed that the end-point mortality has been reached. Observations that are not consistent with end-point mortality are of no value in the context of the detection and measurement of fumigant resistance.

Recommended Methods for the Detection and Measurement of Resistance of Agricultural Pests to Pesticides

Tentative method for adults of some major pest species of stored cereals, with methyl bromide and phosphine — FAO Method No. 16 [1, 2]

Synopsis

A test method is described for detecting and measuring resistance to the fumigants methyl bromide and phosphine in *Sitophilus oryzae*, *S. zeamais*, *S. granarius*, *Rhyzopertha dominica*, *Tribolium castaneum*, *T. confusum*, *Oryzaephilus surinamensis* and *O. mercator*.

The method is based on exposure of adult insects to discrete atmospheres containing fumigant. Exposure periods are 5 hours for methyl bromide and 20 hours for phosphine. Responses are determined 14 days following termination of the exposure.

Base-line data are established with reference strains of known susceptibility from which it is possible to select discriminating doses that may be used to monitor samples of beetles for resistance. Survival in such tests is indicative of resistance, following which extensive testing should be carried out to determine the degree of resistance present.

Equipment and materials

Insectary. Facilities should be available for rearing insects at both 25 and 30°C at approximately 70 percent relative humidity. A large incubator can be used, in which case the humidity can be adjusted by introducing an open tray filled with a saturated solution of sodium nitrate or strontium chloride.

Breeding materials. A summary of the breeding media and appropriate temperatures for the different species is given in Appendix 1. The media should be disinfested by heating in a sealed container at 60°C for one hour after this temperature is reached throughout the medium. For breeding containers, small jars or wide-mouthed bottles sealed with filter paper (Whatman No. 29, black) and paraffin wax (to restrict movement of mites) are suitable. Containers held in the incubator should be placed on trays containing paraffin oil as a further precaution to prevent contamination by mites.

All grain pests are subject to disease in laboratory culture. *Tribolium* species are particularly susceptible to the protozoan parasite *Farinocystis tribolii.* All equipment used for handling insects and media should be sterilized in a hot-air oven at 110 to 120°C between each use and when not in use should be stored in this oven. At least one-half to one hour exposure at this temperature is necessary to ensure the destruction of the protozoan spores. All plastic ware used should be polypropylene, nylon or polycarbonate which is not affected by this temperature.

A supply of Fluon GP1 (an aqueous dispersion of polytetrafluoroethylene, obtainable from Imperial Chemical Industries Ltd.) must be available to assist in restraining all species other than *Tribolium* spp. and *R. dominica.* A film of this material is applied to the top 2 cm of the inside wall of breeding containers to prevent insects congregating on the filter paper

[1] Methods recommended on the basis of an international collaborative study by the FAO Working Party of Experts on Pest Resistance to Pesticides. The Working Party is greatly indebted to R.G. Winks and B. Champ (Australia) for developing this method and to the following for assessment and comments: C.E. Dyte (United Kingdom), E.J. Bond and P.S. Barker (Canada), and D.L. Lindgren and R. Davis (U.S.A.).

[2] See *FAO Plant Prot. Bull.*, 1969, 17(4):76-82 for discussion of general principles.

seals and boring out. All handling containers must be treated similarly.

Test area. A room with normal illumination maintained at 25°C is required. Should this room have a controlled humidity of 70 percent it will also serve to condition the atmosphere of fumigation chambers before commencing tests; however, preconditioning of fumigant chamber atmospheres may be carried out in a breeding room.

Fumigants. Pure methyl bromide (excluding chloropicrin) is recommended. Suitable sources include commercially available ampoules and cans. Aluminium phosphide formulations available commercially provide a suitable source of phosphine.

Glassware, etc.

1. Fumigation chambers. Desiccators, 20 cm (8 in.) in diameter, fitted with a plate of stainless steel or other chemically inert material, and with lids containing ground sockets of a standard glass joint size make suitable fumigation chambers. Cone/screw thread adapters (e.g. Quickfit) should be fitted to the sockets of desiccator lids. A pure gum-rubber septum (or other rubber with good resealing properties when pierced with a syringe needle) is placed under the screw cap. Septa for this purpose are conveniently obtained from sheet rubber 3.2 mm (0.12 in.) thick with a wad punch.

Ground surfaces of desiccator flanges and cone/screw thread adapters should be lightly coated with silicone grease. (The use of cone/screw thread adapters is not essential. Any method providing in the lid of desiccators a septum that ensures both a gas-tight seal and chemically inert surfaces will be satisfactory.)

2. Fumigation cages. Glass rings 30 mm diameter and 25 mm high attached to filter papers (35 mm or 42.5 mm diameter) or small flat-bottom evaporating dishes are recommended as containers in which to confine insects during exposure to fumigant. Stainless steel gauze discs should be placed over fumigation cages when dosing species that may fly.

3. Gas-tight syringes. A range of gas-tight syringes (e.g. Hamilton gas-tight syringes) is required. The range chosen will be influenced by the volumes of the fumigation chambers but would probably include 50, 100 and 250 microlitre syringes together with 1-, 2.5- and 10-millilitre syringes. (It is not good practice to dispense small volumes from a large volume syringe.)

4. Magnetic stirrer. A magnetic stirrer is recommended for stirring gas mixtures wlthin fumigation chambers. For this purpose a 45-mm PVC-coated follower with a rim is placed in the bottom of each fumigation chamber. Where necessary a magnetic stirrer may be made by fitting a suitable magnet to the shaft of a small electric motor. Speed control is not necessary.

5. Fumigant storage vessels. A 25- or 35-ml vial fitted with a screw cap and a Mininert valve[3] provides a satisfactory method for storing methyl bromide (Figure 1). From this vessel, dose volumes of methyl bromide vapour may be obtained with a gas-tight syringe. Alternatively a tube fitted with a septum and side-arm with stopcock, as shown in Figure 1, may be used as a means of providing a source of methyl bromide vapour.

For phosphine, a glass tube fitted with a septum together with a gas jar or measuring cylinder is required. A diagram of this apparatus together with accessory items is shown in Figure 2.

Collection of specimens and rearing

For identification of the various species see Appendix 2. The correct identification of species is particularly important and the tests have been designed to permit workers to identify species after discriminating tests have been conducted. It is essential that all identifications be checked at this time, particularly of sur-

[3] Manufactured by Precision Sampling Corporation, Baton Rouge, Louisiana, U.S.A.

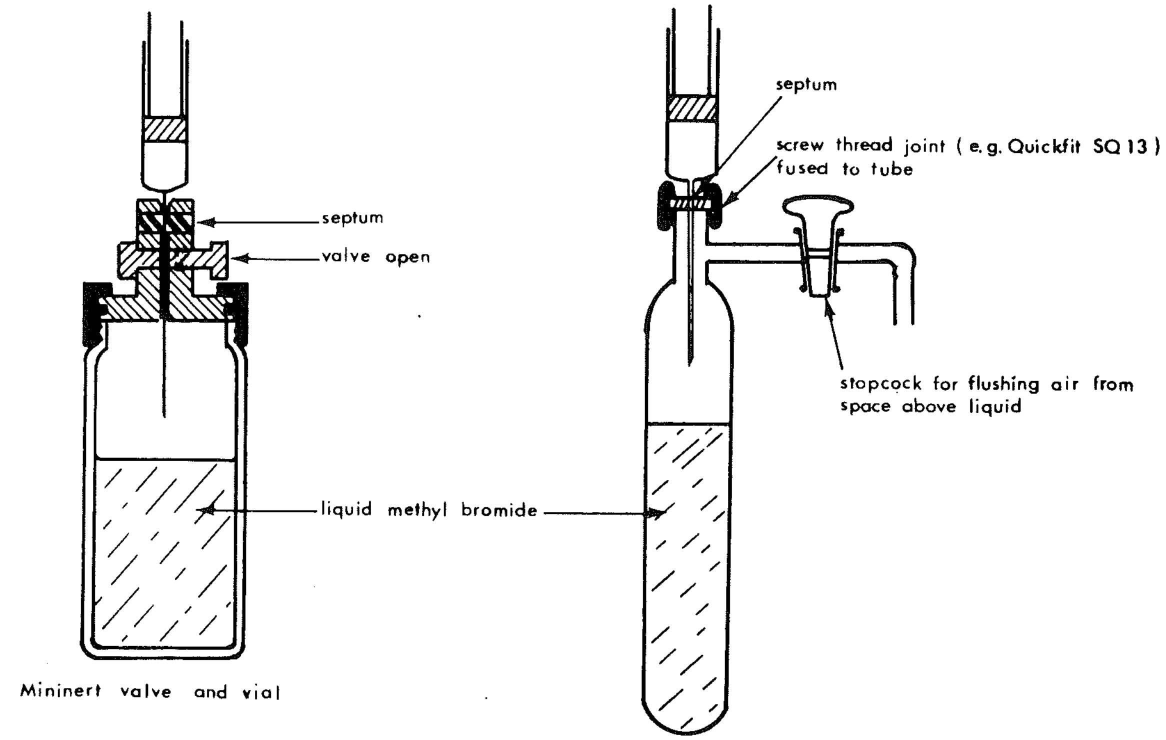


Figure 1. Methyl bromide storage/dose-source vessels.

vivors, and if there is any doubt as to the identity of specimens these should be submitted to an appropriate expert.

Preparation of gas sources

Methyl bromide. All handling of methyl bromide should be carried out in a fume cupboard or well ventilated area. The Maximum Allowable Concentration (MAC)[4] for methyl bromide is 20 ppm.

The container of methyl bromide, the storage vessel (dose-source vessel, see Figure 1) and a small glass funnel should be cooled to about 0°C beforehand. Liquid methyl bromide is then transferred to the storage vessel until it is about three-quarters full, following which the cap of the storage vessel is firmly replaced to ensure a gas-tight seal.

Generally, sufficient methyl bromide will be vaporized during transfer to the storage vessel to flush out most of the air. To expel remaining air from the space above the liquid, the septum should be removed from the Mininert valve when the liquid is at room temperature and the valve opened for a short time allowing gas to escape. If the alternative storage vessel is used, the stopcock in the side-arm is opened for a short time. When not in use, both vessels should be stored in a refrigerator or cool place or in a fume cupboard. Although both vessels should be completely gas-tight the possibility of leakage should not be overlooked.

Phosphine. All handling of phosphine should be carried out in a fume cupboard. The MAC value for phosphine is 0.3 ppm.

Phosphine is conveniently obtained for labo-

[4] The Maximum Allowable Concentration is the maximum concentration of vapour considered safe for a normal eight-hour working day.

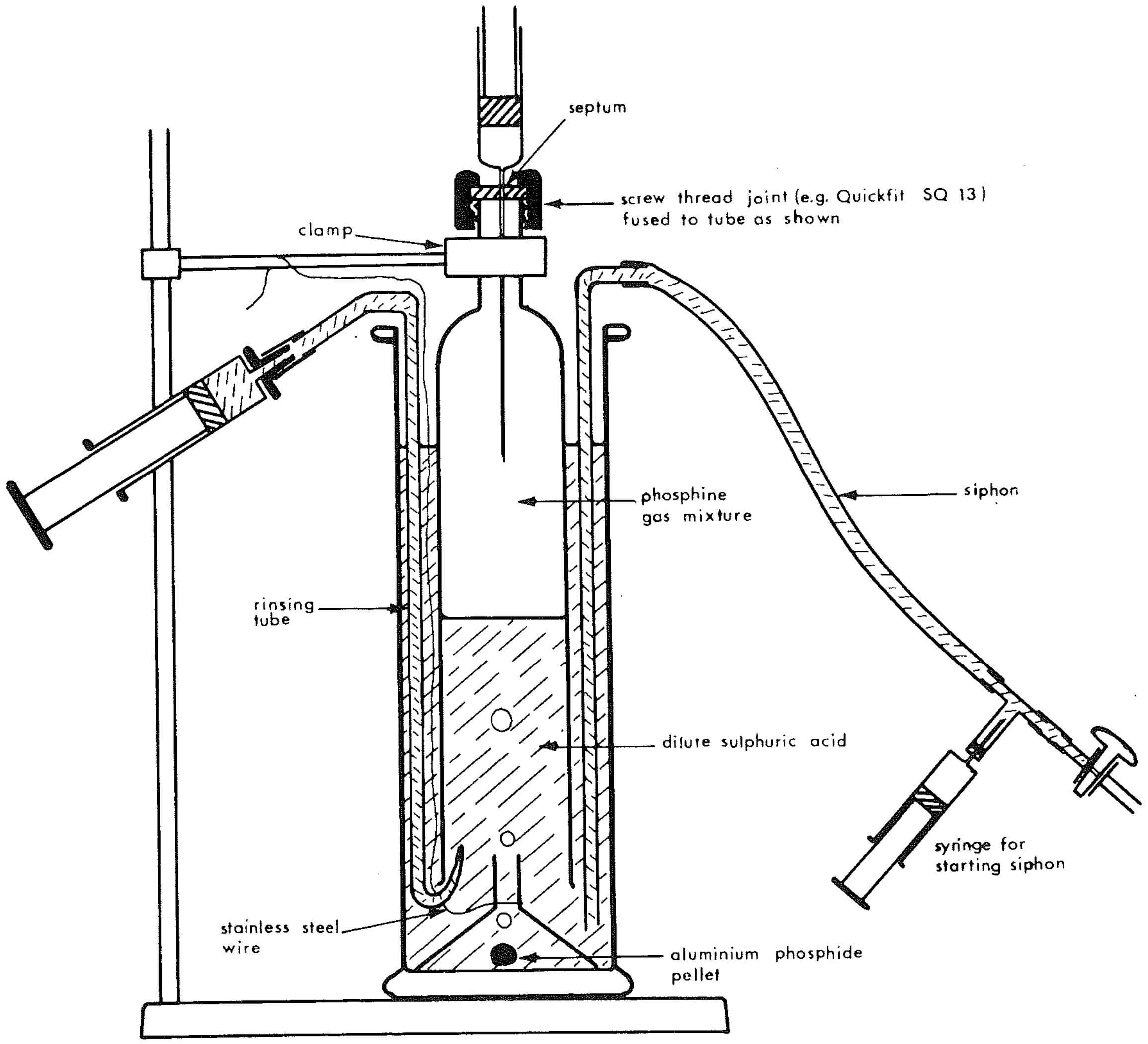


Figure 2. Apparatus for generating phosphine from aluminium phosphide pellets. The collection vessel for phosphine gas mixture is shown inside the gas jar.

ratory dosing purposes from aluminium phosphide according to the equation:

$$AlP + 3HOH \rightarrow Al(OH)_3 + PH_3$$

Some commercially available aluminium phosphide formulations contain ammonium carbamate as well, which also reacts with water liberating ammonia and carbon dioxide.

Commercially available pellets containing a phosphine equivalent of approximately 0.2 g are recommended as the most suitable source of phosphine for the present method.

The apparatus (Figure 2) for generating phosphine is prepared by filling the gas jar, collection tube and rinsing tube with water. All air must be removed from the collection tube and rinsing tube. Approximately half the water in the gas jar is siphoned out and replaced by 10 percent (v/v) aqueous sulphuric acid solution. The contents of the gas jar and collection tube should be thoroughly stirred. Mixing within the collection tube may be achieved by forcing a jet of liquid through the rinsing tube and repeating this procedure a few times. A

pellet containing aluminium phosphide is then placed in the gas jar with the aid of the stainless steel wire, the funnel is lifted slightly and placed over the pellet. Liberation of phosphine commences almost immediately.

As the reaction proceeds, the liquid displaced from the collection vessel is removed by means of the siphon, thus maintaining the level in the gas jar more or less constant. Throughout the procedure the liquid level in the gas jar should be maintained above that in the collection tube thus exerting slight positive pressure on the gas collected.

When the collection tube has been filled with gas, the walls of the tube may be rinsed with the "rinsing tube" to remove adhering pellet residue. This step is not absolutely necessary. However, frequently liquid remains in the neck of the collection tube and this may be displaced by a jet of liquid from the rinsing tube.

The gas mixture obtained in this manner from a "fresh" pellet contains approximately 86 percent phosphine (1.195 hg/μl) and is sufficient to provide a source of phosphine for dosing purposes over several weeks. The inclusion of sulphuric acid in the liquid contents of the gas jar and collection tube is primarily to absorb ammonia but it should also prevent the production of diphosphine (P_2H_4) which is spontaneously inflammable.

Measuring volume of desiccator

The volume of each desiccator must be determined so that dose volumes may be calculated. Thus each desiccator should be fully assembled to simulate operating conditions and then completely filled with water. The weight of water, corrected for the temperature of the water, provides a satisfactory estimate of volume. At 25°C 1 gramme of water occupies 1.003 cc.

Prefumigation procedures

The following procedures are carried out on the day prior to dosing.

Preparation of insect cages. Filter-paper circles are fixed to the bottom of glass rings with a water-soluble adhesive (a film of adhesive in a petri dish facilitates this operation) and the adhesive allowed to dry, preferably in an oven. If the flatbottomed dishes are used, a filter-paper circle of suitable size should be placed in the bottom of the dish so that insects may walk normally.

When testing species that are able to climb a vertical glass surface, rings or dishes should be dipped in liquid Fluon to produce a film approximately 5 mm wide on the upper portion of the inner surface. With dishes it is necessary to provide a ventilation tube to permit displacement of air from inside the inverted dish.

Preparation of insects. A complete test comprises two replicates of 50 insects for each of five concentrations plus two control replicates, i.e. 600 insects in 12 glass rings for each strain tested. Adult beetles are counted in 12 batches of 50 into small vials or directly into the glass rings, progressively placing a maximum of ten insects in each vial or ring until each has the required number. The 12 batches are then assigned at random to the six desiccators, i.e. five treatments plus one control.

When testing species that are inclined to fly, the rings or dishes are covered with a square of stainless steel mesh. The squares of mesh are held in place by pushing down and banding the four corners over the ring or dish.

The insects thus prepared are held overnight in the desiccators, with lids removed, in a controlled temperature environment at 25°C and 70 percent relative humidity.

Determination of dose volumes. The five concentrations to be used in the test should be selected. The data of Appendixes 3 and 5 are intended as a guide to likely dose ranges of susceptible strains. A dose equal to the discriminating dose should be selected as the highest dose of the test.

Having selected the concentrations, the required dose volumes (i.e. gas volumes) are determined (see Appendix 4).

Fumigation procedures

Preparation of chambers. Replace the lids on desiccators within the controlled temperature environment in which the desiccators and insects were held overnight. The atmosphere of the chambers is thus conditioned at atmospheric pressure to 70 percent relative humidity at 25°C. Transfer the desiccators to the dosing area.

Dosing chambers with methyl bromide. If the storage vessel (dose-source vessel) has been stored in a refrigerator, remove the vessel well before dosing is to commence to allow vessel and contents to reach ambient temperature.

Withdraw required gas volumes from the dose-source vessel with the appropriate gas-tight syringe. Flush the syringe, before taking the first dose, by withdrawing small volumes of gas and expelling syringe contents into the fume cupboard. Do not allow heat from the hands to warm the contents of the syringe. Inject the dose into the desiccator and record the time of dosing. Immediately stir the atmosphere of the desiccator with a magnetic stirrer for one to two minutes.

Following dosing, the desiccators should be held at a temperature of 25°C throughout the exposure period. The exposure period required is five hours. This period should be adhered to strictly in normal testing experiments.

Dosing chambers with phosphine. It is advisable to flush syringes to be used for dispensing phosphine doses in a stream of oxygen-free nitrogen immediately before use.

Before taking the first dose with a particular syringe, flush the syringe with small quantities of the phosphine source by withdrawing small volumes of gas and expelling these into the fume cupboard. When drawing phosphine into the syringe move the plunger slowly at all times. A sudden reduction in pressure within the syringe may ignite the phosphine spontaneously. As a further precaution ensure that at all times the liquid level in the gas jar is above that in the collection vessel thus exerting slight pressure on the phosphine gas mixture.

Withdraw the required dose volumes and inject these into the appropriate desiccator, recording the time when each dose is applied. Immediately stir the atmosphere of the desiccator with a magnetic stirrer for one to two minutes. Do not allow heat from the hands to warm the contents of the syringe during the dosing procedure. Between doses syringe needles should be capped with a rubber plug.

Following dosing, the desiccators should be held at a temperature of 25°C throughout the exposure period. The exposure period required for phosphine tests is 20 hours. This period should be adhered to exactly in normal testing experiments.

Post-fumigaticn procedures

Termination of exposure. At the end of the required exposure period the lids of desiccators are removed, insect cages extracted and the desiccators ventilated. All insects are transferred to a small quantity of medium in a suitable container and held at 25°C and 70 percent relative humidity.

Mortality assessment. Mortality should be assessed 14 days from the end of the exposure period. This post-treatment holding period allows time for end-point mortalities to be reached for both fumigants.

Numbers responding, i.e. dead, should be taken to include those insects that are in fact dead together with those showing only slight twitching of appendages when prodded. If death is recorded in the controls, the percentage responding to all test levels should be corrected by Abbott's formula.[5] Results should be discarded and the test repeated if the percentage affected in controls is greater than 10.

Interpretation, calculation and reporting

The mortality figures are plotted on logarithmic-probability paper and the dosage-mortality relationship fitted by eye or by appropriate

[5] See *FAO Plant Prot. Bull.*, 1969, 17:77.

calculations.[6] The LD_{50} and $LD_{99.9}$ values are then determined from these lines. Values are expressed in concentration of fumigant (mg/l) or as concentration × time products (c × t) expressed in milligramme hours per litre (mg h/l). When reporting these values both methods of expression should be prefaced (e.g. in table headings) by a statement of the exposure period since this is the fixed variable of dosage in the tests described.

The above procedures serve to establish baseline data for susceptible reference strains of beetles. Some results obtained by this method are referred to in Appendix 3. Testing of field strains may also be carried out in the foregoing manner. However, when testing field strains a full series of replicates of the susceptible reference strain should be included. Thus chemical estimation of gas concentrations is not necessary. Abnormal gas concentrations during tests will be revealed by the abnormal response of the reference strain. Nevertheless, a detailed evaluation of strains showing increased tolerance may require gas-concentration measurements.

Testing resistant strains

Procedures similar to the above allow the determination of LD_{50} and $LD_{99.9}$ values for resistant strains. It will be necessary to increase dosages to obtain an equivalent range of response. When testing strains resistant to methyl bromide, dosages may be increased by increasing either the concentration or the exposure time. Strains resistant to phosphine, however, should be tested by increasing the fixed period of exposure, e.g. from 20 to 48 hours, and using the same range of concentrations. Small increases in concentrations can be made. At high concentrations of phosphine, however, insects become narcotized, the effect of which is to produce nonlinear probit lines, apparent resistance in susceptible strains and exaggerated resistance factors in resistant strains.

LD_{50} and $LD_{99.9}$ values obtained for resistant strains may be compared with those obtained for the susceptible reference strain and resistance factors calculated.

Monitoring for resistance

For routine monitoring to detect the initial appearance of resistance in wild populations of stored product beetles, it is convenient to use a discriminating dose which is expected to kill all susceptible specimens. The dose chosen is that corresponding to slightly above the $LD_{99.9}$[7] obtained from the regression line for susceptible beetles allowing for, in the case of phosphine, what appears to be inherent variability of response. Some discriminating concentrations are given in Appendix 3. Susceptible reference strains must always be included in discriminating tests.

When using a discriminating test with fumigants it is advisable always to make provision for abnormal concentrations. If a concentration is obtained that is less than the discriminating concentration this will be revealed by abnormal survival in the susceptible reference strain. Abnormally high concentrations may be revealed by the inclusion in the tests of a reference strain (or species) with slightly greater tolerance to the fumigant than the susceptible reference strain on which the discriminating dose is based, approximately × 1.5 for methyl bromide tests and × 2.5 for phosphine tests. An alternative approach to this is to use three concentrations, one at the discriminating concentration, one at the approximate LC_{90} level and the other at an equivalent level above the discriminating concentration.

In regular monitoring for resistance, it is desirable that it may be detected when only a small proportion of resistant individuals is present. For such purposes a minimum of 100

[6] Finney, D.J. 1971. *Probit analysis.* 3rd ed. London, Cambridge University Press.

[7] If the graph paper used does not go up beyond 98 percent kill, the increased dose corresponding with 99.9 percent kill can be found in the following way: (assuming that logarithmic-probability paper is used) the concentration corresponding with 84.5 percent is read from the regression line and the amount of difference from the 98 percent kill concentration is *added* to the latter.

insects in two batches of 50 should be used per sample.

Limited numbers of insects may not be sufficient to detect low levels of resistance. Therefore, additional samples should be obtained if possible. If, however, there is suspicion of serious resistance (e.g. from failure of treatments) a test with small numbers (10 to 20) may provide early valuable indication.

The insects are exposed to the discriminating dose for the appropriate period, in the usual way. If all of them are dead at the end of the post-treatment holding period, the sample can be classified as "no resistance detectable", and the medium in which they were held is put into a hot-air oven to destroy the culture. On the other hand, the presence of unaffected insects at the end of the test should be regarded as *prima facie* evidence of resistance, requiring further investigation.

Confirming resistance when a few insects are unaffected

The appearance of unaffected insects in a discriminating test could be due to the presence of unusually tolerant individuals from a normal population. Provided that the conditions of exposure, the physiological state of the insects and the dosages are consistent, the probability of a single insect in a batch of 100 being unaffected due to chance is less than 0.1 (i.e. less than once in ten tests). It is important to determine whether incomplete response is due to such causes or to genuine resistance. This can be checked in the following manner:

1. By repeating the test, using further samples from the same field population. The chances of adventitious failure to respond by a single individual in each of successive tests decline progressively (less than 0.01, 0.001, 0.0001 and so on). Survival of two or more individuals throughout is even less likely. Therefore, the continued appearance of a proportion of unaffected individuals can be considered as proof of resistance.
2. Alternatively, the insects which were unaffected in the discriminating test may be kept and used for breeding a further generation. Should their reaction be truly due to resistance, it will be found that a substantially larger proportion of their progeny will fail to respond to the discriminating concentration.

Appendix 1

REARING TEMPERATURES, MEDIA AND APPROXIMATE TIMES OF DEVELOPMENT FOR THE TEST SPECIES

Insect	Rearing temperature	Rearing medium	Rearing times		
			First emergence	Peak emergence	Progeny removed
			Days		
Sitophilus oryzae	25°C	Wheat	35	36-43	63
S. zeamais	25°C	Wheat	35	36-43	63
S. granarius	25°C	Wheat	34	36-43	63
Rhyzopertha dominica	30°C	Wheat + broken wheat (3:1)	35	36-43	63
Tribolium castaneum	30°C	Wholewheat flour + yeast (12:1)	23	26-30	42
T. confusum	30°C	Wholewheat flour + yeast (12:1)	27	29-32	42
Oryzaephilus surinamensis	25°C	Broken wheat + rolled oats + yeast (5:5:1)	26	28-32	42
O. mercator	25°C	Broken wheat + rolled oats + yeast (5:5:1)	26	28-32	42

Appendix 2

IDENTIFICATION OF SPECIES CONCERNED

Sitophilus spp.

The *Sitophilus* spp. (Figure 3) are distinguished from most other stored product beetles in that the head is elongated in front of the eyes to form a well-defined rostrum or snout and the antennae are elbowed and clubbed.

S. oryzae is a dark brown species, 2.3 to 3.5 mm long with fully developed hindwings and two reddish-yellow markings on each wing cover. The prothorax is densely covered with round or irregularly shaped punctures.

S. granarius is larger than *S. oryzae* being 3 to 4 mm long. It has a dark brown, shining appearance, does not have hindwings and does not have lighter-coloured spots on the wing covers. The prothorax is covered with oval to oblong punctures.

S. zeamais is the largest *Sitophilus* spp., being 3 to 4.5 mm long. It very closely resembles *S. oryzae* in colour and shape though usually they may be distinguished by the larger size of *S. zeamais*. Positive identification must be made from the aedeagi of males. In *S. oryzae* the apex of the basal sclerite is rounded, the curve of the aedeagus is more or less uniform to the tip and the upper surface of the aedeagus is evenly convex, while in *S. zeamais* the apex of the basal sclerite is extended and angular, the tip of the aedeagus is distinctly hooked and the upper surface of the aedeagus flattened with two distinct longitudinal grooves. In females of *S. oryzae* the arms of the Y-shaped sclerite are not tapered and have rounded ends while in *S. zeamais* they are tapered to points.

Rhyzopertha dominica

Rhyzopertha dominica (Figure 4) adults are small, cylindrical brown beetles, 2.5 to 3.0 mm long.

The head is deflexed and more or less concealed from above by the prothorax which, particularly anteriorly, is densely covered with coarse tubercles.

Oryzaephilus spp. (Figure 5)

Adults are small, elongated brown beetles, 2.5 to 3.5 mm long, with six large teeth spaced along each lateral margin of the prothorax. The disc of the prothorax has three longitudinal ridges.

O. surinamensis may be distinguished from the closely related oil-seed pest *O. mercator* by the length of the temple of the head (region directly behind the eye) which is equal to or greater than half the vertical diameter of the eye in *O. surinamensis* and much less than half the vertical diameter in *O. mercator*.

Tribolium spp. (Figure 6)

The species of *Tribolium* concerned in the tests are characterized by the presence of distinct parallel ridges on the wing covers and by eyes which are always partly divided by the side margin of the head with their vertical diameter greater than the horizontal.

T. castaneum adults are reddish-brown beetles, 2.3 to 4.4 mm long. They can be distinguished from *T. confusum* adults by the three-segmented antennal club and the distance between the eyes on the underside of the head, which is much less than two eye widths.

T. confusum adults closely resemble *T. castaneum* adults in colour, shape and size, being 2.6 to 4.4 mm long. The antennae are gradually thickened toward the apex and the distance between the eyes on the underside of the head is equal to three eye widths. The ridge above the eyes is much more distinct than in *T. castaneum*.

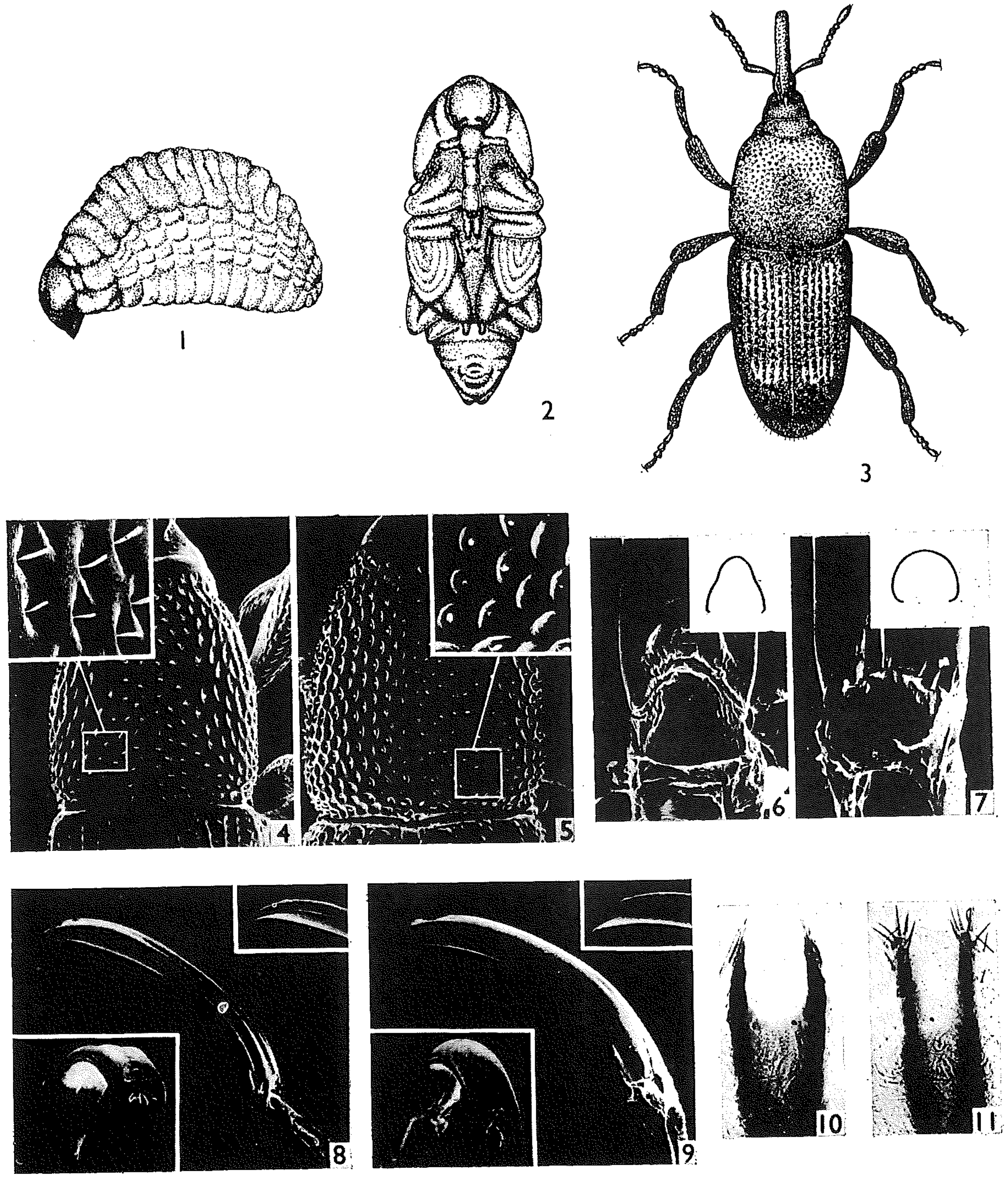


Figure 3. Sitophilus spp. *S. oryzae.* — 1. Larva. 2. Pupa. 3. Adult. *S. granarius.* — 4. Punctations on prothorax. *S. oryzae.* — 5. Punctations on thorax. *S. zeamais.* — 6. Basal sclerite of aedeagus. *S. oryzae.* — 7. Basal sclerite of aedeagus. *S. zeamais.* — 8. Aedeagi. *S. oryzae.* — 9. Aedeagi. *S. zeamais.* — 10. Y-shaped sclerite of female. *S. oryzae.* — 11. Y-shaped sclerite of female.

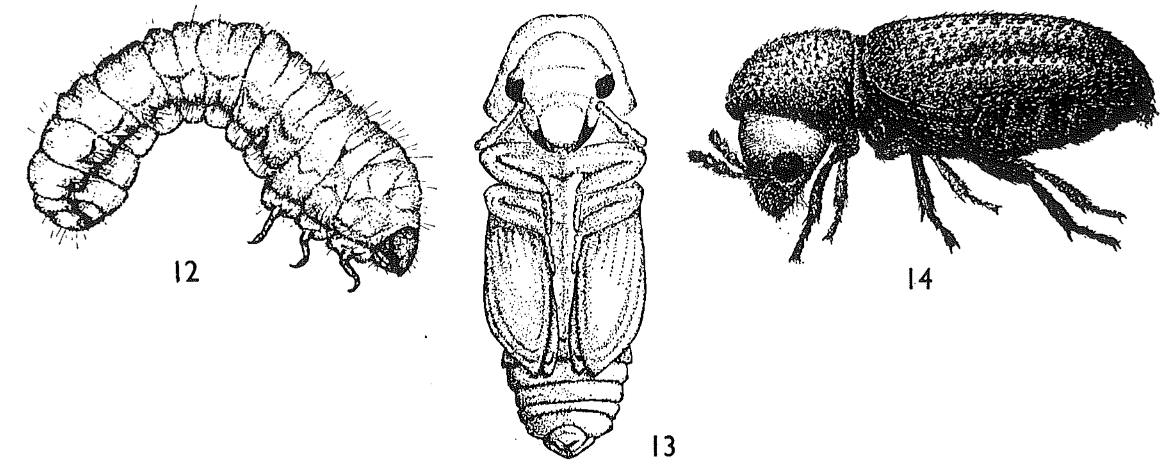


Figure 4. Rhyzopertha dominica F. 12. Larva. 13. Pupa. 14. Adult.

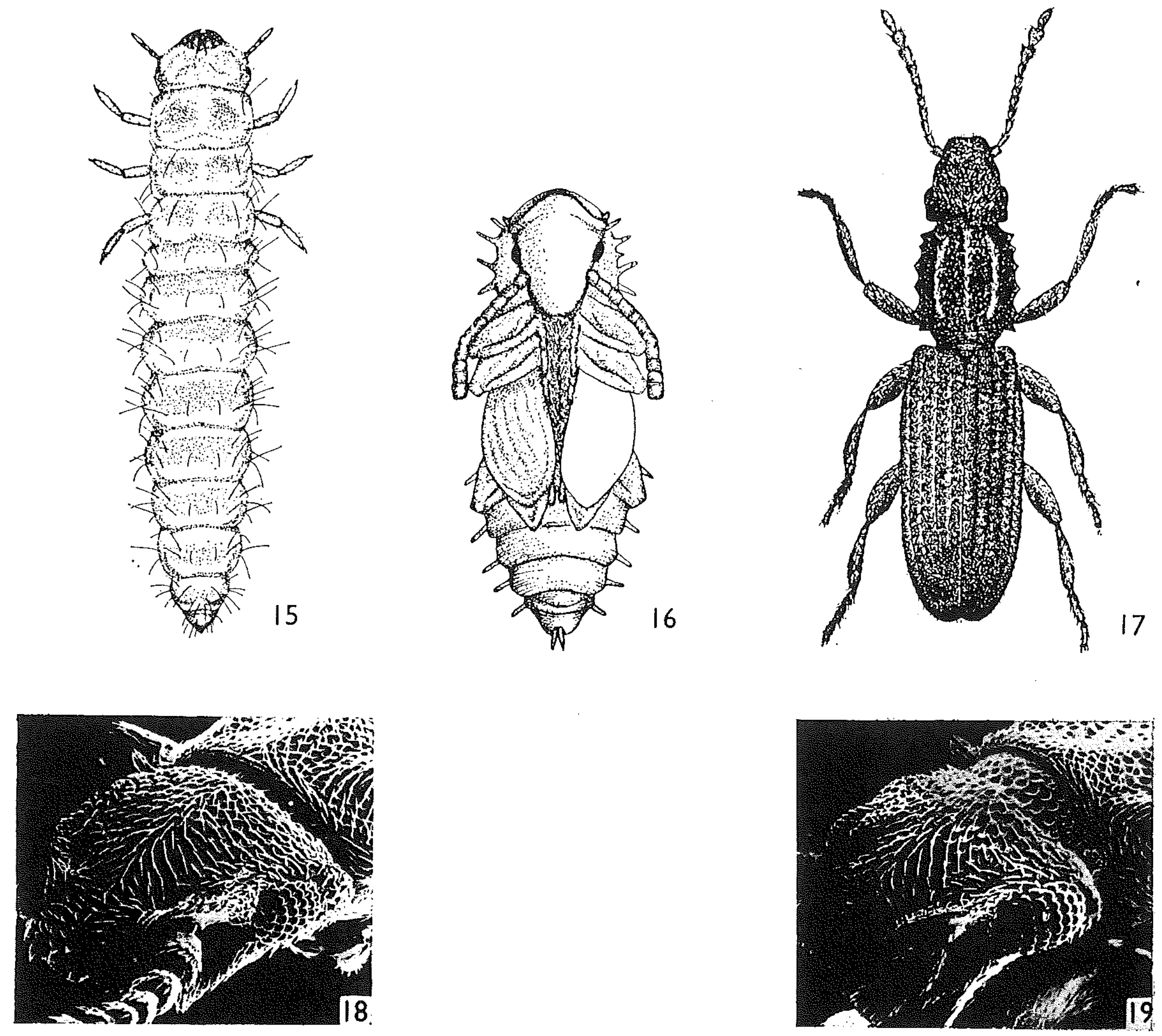


Figure 5. Oryzaephilus surinamensis and *O. mercator. O. surinamensis.* — 15. Larva. 16. Pupa. 17. Adult. 18. Eye and temple of head. *O. mercator.* — 19. Eye and temple of head.

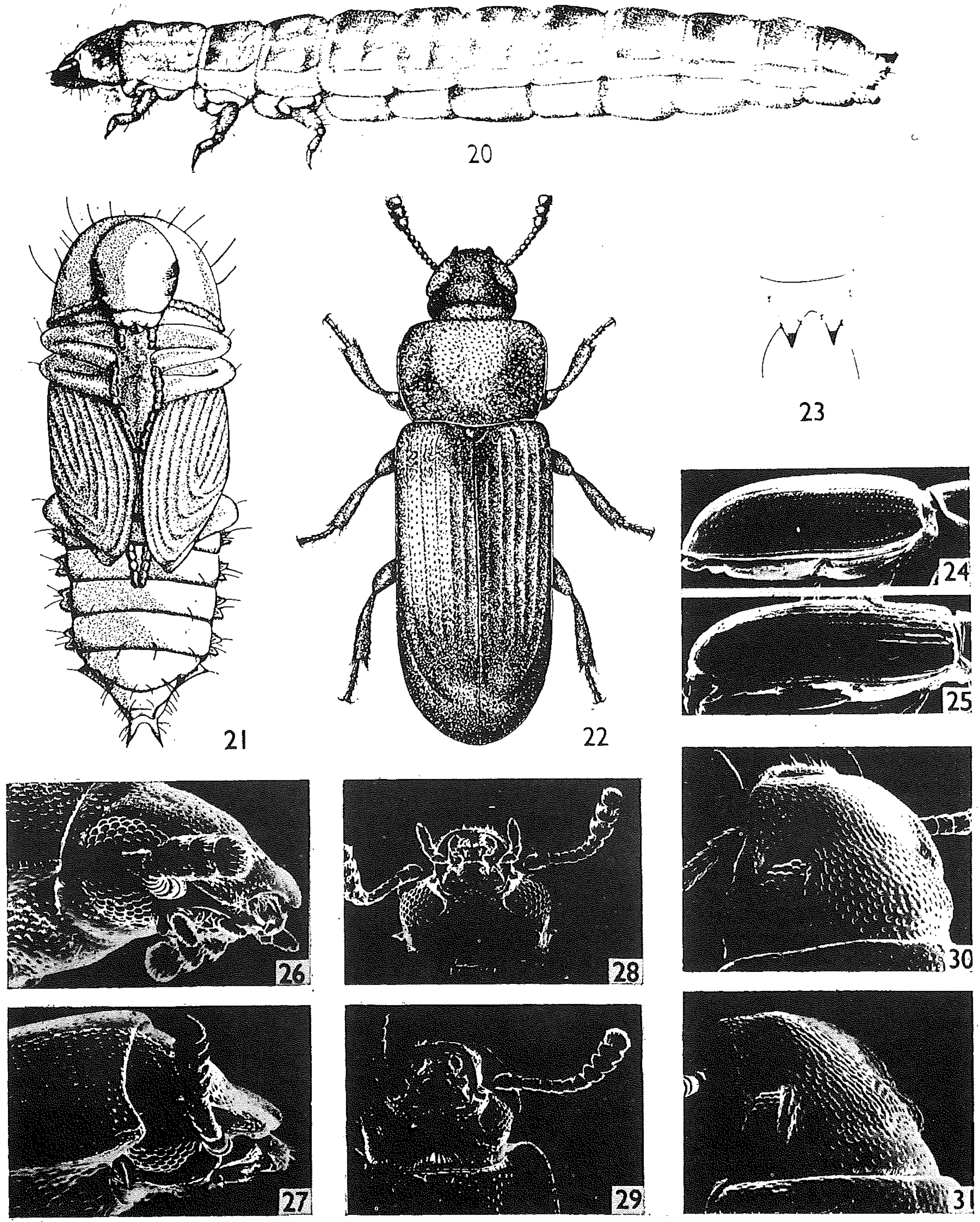


Figure 6. *Tribolium* spp. and some related genera with which they may be confused. *T. castaneum.* — 20. Larva. 21. Pupa. 22. Adult. 23. Dorsal view of terminal abdominal segments of larva. *Gnathocerus.* — 24. Ridges on wing covers. *Tribolium.* — 25. Ridges on wing covers. 26. Eye and side margins of head. *Palorus.* — 27. Eye and side margins of head. *T. castaneum.* — 28. Antennae and underside of head. *T. confusum.* — 29. Antennae and underside of head. *T. castaneum.* — 30. Ridge above eye. *T. confusum.* — 31. Ridge above eye.

Appendix 3

SOME NORMAL SUSCEPTIBILITY DATA OBTAINED FOR METHYL BROMIDE AND PHOSPHINE TOGETHER WITH DISCRIMINATING CONCENTRATIONS

	LC_{50}	$LC_{99.9}$	Discriminating concentration
	......	*mg/l*	......
METHYL BROMIDE			
(Exposure period 5 hours)			
Sitophilus oryzae	3.6	4.8	6
S. zeamais	3.2	5.4	6
S. granarius	5.1	7.5	9
Rhyzopertha dominica	4.0	7.4	7
Tribolium castaneum	8.4	11.7	12
T. confusum	8.6	11.2	13
Oryzaephilus surinamensis	5.8	8.5	9
O. mercator	5.8	8.5	9
PHOSPHINE			
(Exposure period 20 hours)			
Sitophilus oryzae	0.011	0.039	0.04
S. zeamais	0.007	0.013	0.04
S. granarius	0.013	0.041	0.07
Rhyzopertha dominica	0.008	0.028	0.03
Tribolium castaneum	0.009	0.028	0.04
T. confusum	0.011	0.029	0.05
Oryzaephilus surinamensis	0.012	0.036	0.05
O. mercator	0.011	0.034	0.05

Appendix 4

CALCULATIONS OF DOSE VOLUMES AND CONCENTRATIONS

The method requires the selection of concentrations, following which dose volumes of gas are determined. The following examples show the calculations and steps required to determine dose volumes and actual concentrations for a temperature of 25°C (298°K).

Example 1. Methyl bromide

Step 1. Determine the volume, d_1(ml) of methyl bromide vapour at 25°C required to obtain a concentration of x_1(mg/l) in a desiccator of volume V_1(l).

$$\frac{298 \times x_1(\text{mg/l}) \times V_1(\text{l}) \times 22.414 \times 1\,000}{273 \times 1\,000 \times 94.939 \text{ (GMW methyl bromide)}} = d_1(\text{ml})$$

i.e. $x_1(\text{mg/l}) \times V_1(\text{l}) \times 0.2577 = d_1(\text{ml})$

Step 2. Select nearest whole division on appropriate syringe to give actual dose volume D_1(ml) of vapour and recalculate concentration, i.e. concentration X_1(mg/l) actually applied.

$$\frac{D_1(\text{ml}) \times 273 \times 94.939 \times 1\,000}{298 \times V_1(\text{l}) \times 22.414 \times 1\,000} = X_1(\text{mg/l})$$

$$\text{i.e. } \frac{D_1(\text{ml}) \times 3.8804}{V_1(\text{l})} = X_1(\text{mg/l})$$

Example 2. Phosphine

Step 1. Determine the volume d_1(µl) of the 86% phosphine gas source at 25°C required to obtain a concentration of x_1(mg/l) in a desiccator of volume V_1(l).

$$\frac{298 \times x_1(\text{mg/l}) \times V_1(\text{l}) \times 22.414 \times 1\,000 \times 1\,000 \times 100}{273 \times 1\,000 \times 33.9977 \text{ (GMW phosphine)} \times 86} = d_1(\mu\text{l})$$

i.e. $x_1(\text{mg/l}) \times V_1(\text{l}) \times 836.81 = d_1(\mu\text{l})$

Step 2. Select nearest whole division on appropriate syringe to give actual dose volume D_1(µl) of the 86% phosphine source and recalculate concentration, i.e. concentration X_1(mg/l) actually applied.

$$\frac{D_1(\mu\text{l}) \times 273 \times 1\,000 \times 33.9977 \times 86}{298 \times V_1(\text{l}) \times 22.414 \times 1\,000 \times 1\,000 \times 100} = X_1(\text{mg/l})$$

$$\text{i.e. } \frac{D_1(\mu\text{l}) \times 0.001195}{V_1(\text{l})} = X_1(\text{mg/l})$$

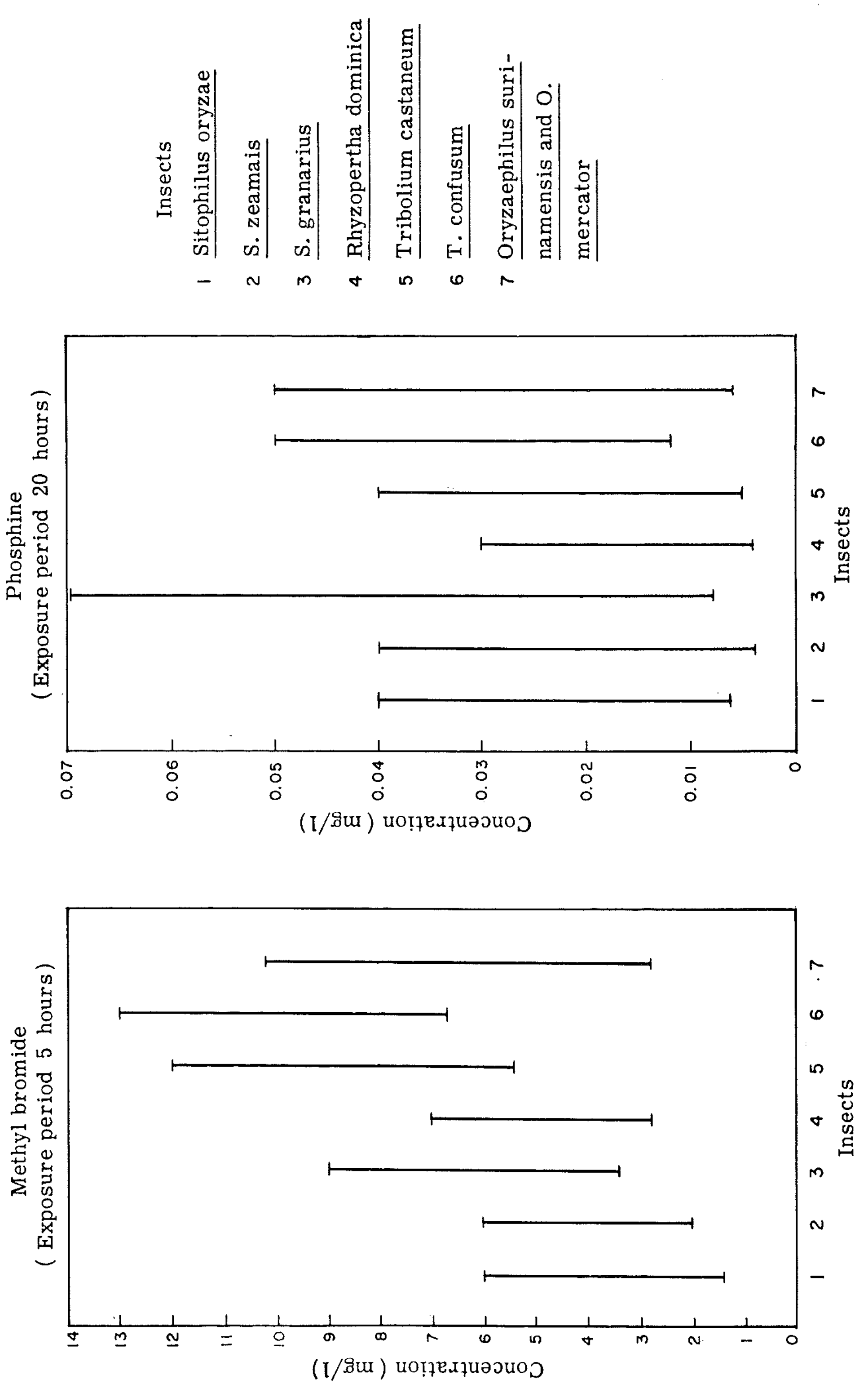
An 86% phosphine source is equivalent to a concentration of 1.195 µg/µl. Thus if concentration is expressed in terms of (µg/l) the equivalent of steps 1 and 2 in the foregoing is given by

Step 1 $$\frac{x_1(\mu\text{g/l}) \times V_1(\text{l})}{1.195\ (\mu\text{g}/\mu\text{l})} = d_1(\mu\text{l})$$

Step 2 $$\frac{D_1(\mu\text{l}) \times 1.195}{V_1(\text{l})} = X_1(\mu\text{g/l})$$

Appendix 5

SUGGESTED CONCENTRATION RANGES FOR TESTS ON SUSCEPTIBLE BEETLES



Appendix 2

Form of Notice of Impending Fumigation

Schedule No. 1

Notice of Intention to Conduct a Fumigation[1]

To: ....

....[2]

Please take notice that it is my intention to fumigate[3]

....

by means of[4] ....

on .... commencing at .... o'clock a.m./p.m.

Date .... Signed ....
(Authorised Fumigator)

Notes to Occupier:

1. You are required to vacate the area before fumigation as instructed and not return until advised that the area is safe for re-entry.
2. You are required to acknowledge receipt of this notice by signing the duplicate hereof.

Date .... Signed .... (Occupier)

Notes on the form:

1. The design and wording of this form should take into account the relevant requirements of local legislation.
2. This form should be sent to the appropriate authority, the nearest Police Station and Fire Brigade,and every tenant or occupier within the fumigation and risk area who must acknowledge receipt by signing a duplicate copy which shall be retained by the fumigator.
3. Here state name or number and location of building, vessel, or other enclosed space intended to be fumigated.
4. Here insert name of fumigant to be used.

Appendix 3

Form of Notice to be Affixed to Premises Undergoing Fumigation

DANGER–KEEP OUT
POISON GAS
FUMIGATION WITH [NAME OF FUMIGANT USED]

Fumigator:....................................

Contact Address:.............................

....

Telephone:....................................

Date of Fumigation:..........................

Appendix 4

Form of Clearance Notice Following Completion of Fumigation

Certificate of Clearance[1]

[Name of fumigant used] Fumigation

To the officer-in-charge of the grain store at ....

.... I, being the officer-in-charge of the

fumigation of ....

....,

hereby declare that I am satisfied that the risk area is free from danger arising from the use of the fumigant. I make this declaration after having examined the area and tested for fumigant in the atmosphere in the working spaces and cell top spaces/over grain spaces.

Signature of fumigator ....

Date: ....

Time: ....

The above Certificate of Clearance was handed to me at ....

on ....

Signature of officer in charge of the premises:

....

Note on the form:

1. The design and wording of this form should take into account the relevant requirements of local legislation.

Appendix 5

Methods for determining the degree of gastightness of structures[1]

The three tests available for determining the level of gastightness of enclosures are:

- pressure decay test ('Pt test')
- equilibrium pressure-flow test ('PQ test')
- tracer decay test.

In general, the 'Pt test' is to be preferred as it uses simple apparatus, is independent of structure volume, and usually takes less than an hour to perform.

The 'PQ test' is useful where an estimate of the actual leak size is required, or the gastightness of a series of identical enclosures (e.g. freight containers) is to be accurately compared. It is slower (taking perhaps 2 or 3 hours) and more complex to carry out.

The tracer gas test takes several days to carry out and is useful in normal practice only in special circumstances where the other methods cannot be used. This applies for very large or very leaky structures and for some flexible and fragile ones. Tracer tests are also useful in research to confirm that a standard set using Pt or PQ tests, in fact, corresponds to suitable gas loss rate.

The instructions which follow are for testing structures of up to 2000 tonnes capacity.

Pt tests

Apparatus required

- A fan capable of delivering 3 cubic metres per minute of air at 1000 Pa (e.g. Hoover upright heavy duty model vacuum cleaner)
- A stopwatch
- A pressure measuring device (e.g. Dwyer inclined manometer or Magnahelic pressure guage, to read up to 1000 Pa)
- A 5 cm (2") diameter ball valve
- A quantity of 5 cm (2") diameter plastic hosing (capable of withstanding 3000 Pa without collapse if vacuum testing is to be used).

Procedure

Before making the test decide on whether vacuum or pressure should be used and on the upper pressure limit. Pressure decay should normally be used, but flexible structures should be tested by vacuum decay. The upper pressure or vacuum limit should be as high as possible to minimise thermal effects and, of course, consistent with the strength of the structure. In general, +500 Pa is a suitable upper limit, but +100 Pa may be as much as some structures and sealing methods can take without damage. Welded steel cells and concrete silos may be able to take +1500 Pa, and higher pressures are unnecessary.

1. See, for example, Zahradnik (1968) for a more comprehensive coverage of gastightness testing methods.

If in doubt as to the pressure that can be used without damage, seek advice from a qualified structural engineer. Set the lower pressure limit to be half the upper one.

Connect the fan to the enclosure with the plastic hosing and with the ball valve in line in the hosing. The fan should be either blowing air into, or extracting it from the enclosure as appropriate. Ensure there are no leaks at the ball valve and where the hosing enters the enclosure under test. There should be no restrictions between the fan and the enclosure. Connect the pressure sensor to another part of the enclosure using 6 mm (1/4") plastic tubing. Run the fan with the valve open until the pressure differential exceeds the upper pressure limit for the decay by 10%. Shut the ball valve quickly and time the decay between the upper and lower pressure limits.

Presentation of results

Quote the results as the time taken for the pressure to fall between the two pressure limits and record the limits used. If possible use the same limits each time the particular enclosure is tested. For research purposes it is useful to record the complete decay curve as in Figure C1.

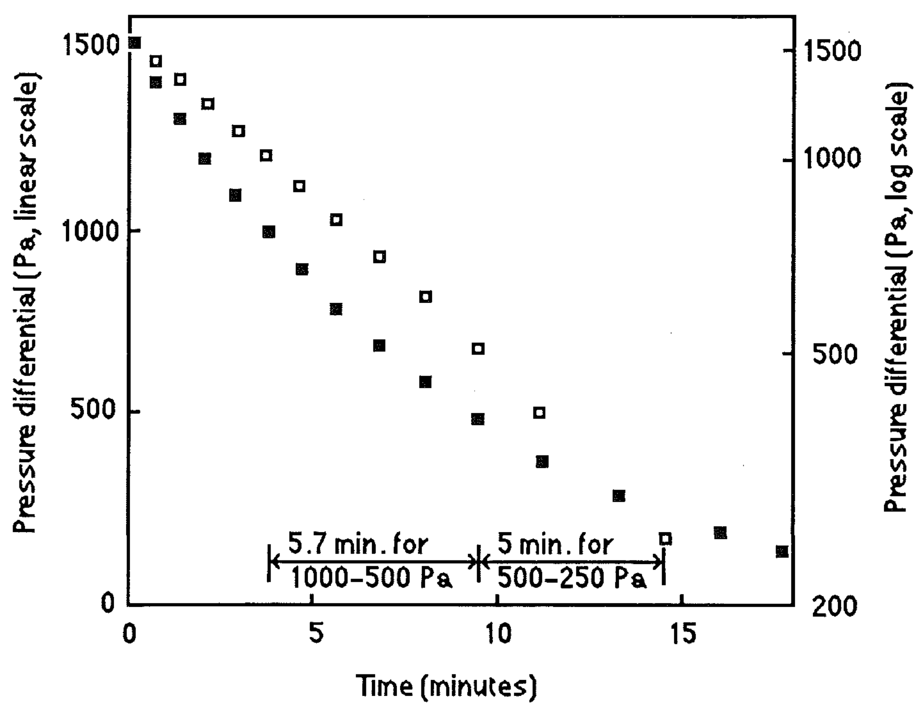


Fig. C1. Idealised pressure decay curves (artificial data) on linear (■) and logarithmic (□) coordinates for a 2000 tonne storage.

PQ tests

Apparatus

As for Pt tests, a fan, valve, hosing, and pressure sensor are required. Also needed for PQ tests is a gas flow meter (e.g. Rotameter). The capacity of the flow meter needed varies with the size of the enclosure under test. It is often convenient to have made a bank of flow meters, which gives a range of flow measurements from 0.005 to 3 cubic metres per minute, in order to accommodate widely varying requirements and give a wide range of test flows. An adjustable rheostat (e.g. Variac) is useful for regulating the speed of the fan if it has a brush motor.

Procedure

Connect as for Pt test, but with the flow meter in line between the fan and valve. Run the fan and adjust the gas flow, either by a rheostat on the fan or by the valve, until the maximum pressure limit (see Pt test) is obtained. Observe the flow rate when the pressure is in equilibrium, neither rising nor falling appreciably. With large but well sealed structures this equilibrium may take several minutes to establish. Repeat this process for a series of pressures each 0.6× the previous one. At least four pressures should be used.

Presentation of results

Plot the natural logarithm of the flow rate, $\ln Q$, against the natural logarithm of the corresponding equilibrium pressure, $\ln \Delta p$. This should give a linear relationship. Calculate the slope (n) and intercept $(\ln b)$ of this graph. This may most easily be carried out using regression analysis on a programmable calculator.

Quote calculated values of b and n and also the flow rate corresponding to a standard equilibrium pressure, e.g. 100 Pa or 250 Pa. The latter may be obtained by interpolation from the $\ln Q$ - $\ln \Delta p$ graph.

C.3.4.3. Tracer decay tests

Apparatus

- A source of gas and gas measurement equipment capable of measuring gas concentrations over at least 50× range (e.g. Dräger tubes)
- Nylon gas sampling line (c. 2 mm i.d.)
- Scales to weigh accurately in the kilogram range or flow meter taking a few litres a minute (e.g. Gapmeter).

Procedure

Select a tracer gas which can be easily measured with available apparatus and which does not react appreciably with commodities in the enclosure. Carbon monoxide is an ideal tracer gas for this purpose, but phosphine or carbon dioxide

may also be used. Carbon dioxide gives a somewhat higher value than the true value for gases of the same density as air because of the 'stack' effect. Because phosphine is sorbed on grains to some extent, the rates of loss measured are higher than the true value. Most other fumigants are not suitable as they are strongly sorbed on commodities. Rig at least two gas sampling lines within the enclosure and lead these out to a sampling station point in a safe, well ventilated region. One point should be in the headspace and one in the commodity bulk, preferably at about its centre.

For carbon monoxide, introduce enough gas from a cylinder to produce about 100 ppm v/v in the structure. For large quantities, this can be done by weight as with methyl bromide. For small quantities use a flow meter.[2]

After a 24 hour initial period to allow concentrations to become even, sample the gas concentration within the enclosure at least twice a day at each point over a 7 day period. Note: carbon monoxide is highly toxic to man (TLV = 50 ppm); it is odourless and in some concentrations in air is explosive. Users should familiarise themselves with its properites before attempting this test.

With carbon dioxide, add enough gas to give an easily measured concentration (e.g. 20% for Dräger tubes). Observe as for carbon monoxide.

With phosphine, add enough phosphine-generating tablets on the commodity surface (with the usual precautions) to give at least 1 g/m^3 of gas. After a 5 day period to allow the gas to evolve, observe the gas concentration as with carbon monoxide.

Presentation of results

Graph the observations as natural logarithms of concentration against time in days. This line should be approximately linear but will have some scatter due to changing weather conditions. With carbon dioxide, the curve may be slightly convex towards the origin. Calculate or measure the slope of the semilogarithmic plot (k) and quote this as a percentage volume interchange rate (i.e. slope (k) x 100). Note the gas used. Phosphine will give similar results to carbon monoxide in empty enclosures, but because of sorption, will give about +5% to +15% volume interchange rate per day compared with carbon monoxide in filled enclosures.

2. The concentration of CO (in ppm) is given by:

$$x/(\rho \cdot V\ 10^6) \text{ or } Qt/(V \cdot 10^6)$$

where x is mass added (kg), Q is the flow rate of addition (m^3/s) for time t (sec.), and V is the enclosure volume after correction for the exclusion volume of the commodity. Jones (1943) gives a useful table of exclusion volumes for various grains and pulses.

Appendix 6
Calculation of Ct products

Effective fumigation with methyl bromide can be ensured only if the recommended Ct product has been reached or exceeded. The Ct product is calculated by multiplying the concentration of fumigant observed in grams per cubic metre (g/m^3) by the time in hours (h) that the concentration has been present, and is recorded in gram hours per cubic metre (g h/m^3). If the gas concentration within the enclosure were to remain constant, the Ct product could be estimated simply by multiplying the concentration by the exposure time. However, in any real fumigation the gas concentration always changes with time. The Ct product then has to be calculated by adding together the component Ct products obtained from the average concentration of sequential observations and multiplying by the time interval between them. *The best approximation of true total Ct product is obtained with a large number of concentration observations in an exposure.* However, practical constraints often limit the number of observations that can be made. Concentrations should be measured at about 2, 4, 12, and 24 hours after dosing. If a 48-hour exposure is used, readings at about 36 and 48 hours should also be taken. A Ct product cannot be calculated on fewer than two concentration measurements. If only two readings are possible the first must be taken after gas mixing is complete and the second must indicate a quantifiable concentration (that is, more than zero or a trace).

In fumigations under gas-proof sheeting where gas loss rates are very high, the Ct product is best calculated by using the geometric mean. This is done by multiplying together two observed gas concentrations (as grams per cubic metre), taken one after the other then multiplying the square root of this number by the time interval (in hours) between the two readings. This can be expressed as the equation:

$$Ct_{n,n+1} = (T_{n+1} - T_n) \times \sqrt{C_n \times C_{n+1}} \quad (\text{g h/m}^3) \qquad (1)$$

where

T_n is the time the first reading was taken in hours

T_{n+1} is the time the second reading was taken in hours

C_n is the concentration reading at T_n in g/m^3

C_{n+1} is the concentration reading at T_{n+1} in g/m^3

$Ct_{n,n+1}$ is the calculated Ct product between T_n and T_{n+1} in g h/m^3

The Ct products obtained from a series of readings may then be added to calculate the cumulative Ct product for the whole exposure period (see examples 1 and 2 in this Appendix). It is this value that is used to indicate the success or failure of a fumigation. The calculation is easily carried out on a simple electronic calculator with a square root function.

In well sealed enclosures that have passed a pressure test where gas loss rates are low, the Ct product may be calculated by using the arithmetic mean. This is done by adding together two observed gas concentrations (as grams per cubic metre), taken one after the other, and multiplying half of this number by the time interval (in hours) between the two readings. This can be expressed as the equation:

$$Ct_{n,n+1} = \frac{(T_{n+1} - T_n) \times (C_n + C_{n+1})}{2.0} \quad (\text{g h/m}^3) \qquad (2)$$

where:

T_n is the time the first reading was taken in hours

T_{n+1} is the time the second reading was taken in hours

C_n is the concentration reading at T_n in g/m^3

C_{n+1} is the concentration reading at T_{n+1} in g/m^3

$Ct_{n,n+1}$ is the calculated Ct product between T_n and T_{n+1} in g h/m^3

The Ct products obtained from a series of readings may then be added to calculate the cumulative Ct product for the fumigation (see example 3). It is this value that is used to indicate the success or failure of a fumigation.

It is possible to add gas during the course of an exposure to maintain a minimum gas concentration and so achieve a prescribed or statutory Ct product.

Note: whichever method of calculating the Ct product is used, it is important the gas within the enclosure is well mixed and the concentrations have become approximately even by the time the first concentration reading used in the calculation (e.g. 2 hours in a bag stack) have been taken. Pairs of observations containing a zero or unquantifiably low (e.g. trace) concentration cannot be used to obtain a valid contribution towards a cumulative Ct product.

Worked examples of Ct calculation

The following examples (based on hypothetical methyl bromide fumigations) are given to illustrate the steps needed to calculate Ct products using either equation 1 or 2 above.

Example 1

A fumigation under gas-proof sheets with a high loss rate, where the Ct product is calculated on the basis of equation 1. This is the type of result that would be expected in many commercial fumigations or where the commodity is very sorbtive.

Readings:

Time (hours)	Time step (hours)	Concentration (g/m^3)	Ct product ($g\ h/m^3$)	Cumulative Ct ($g\ h/m^3$)	Comments
0.0	-	-	-	-	End of gassing
2.0	2.0	20.0	†	0.0	Ct cannot be calculated
4.0	2.0	15.5	35.2	35.2	
12.0	8.0	6.2	78.4	113.6	
24.0	12.0	2.0	42.3	155.9	
36.0	12.0	trace	*	155.9	Ct cannot be calculated
48.0	12.0	0.0	*	155.9	Ct cannot be calculated

†No contribution to Ct as gas most probably not mixed by this time and sample may not be representative of concentrations as a whole.
*Ct for this time period cannot be calculated as final value is less than a quantifiable concentration.

Example of calculation

Using equation 1 for the period from 2 to 4 hours

$$Ct_{2,4} = (4.0 - 2.0) \times \sqrt{(20.0 \times 15.5)}$$
$$= 2.0 \times \sqrt{310.0}$$
$$= 2.0 \times 17.6$$
$$= 35.2$$

That is, the Ct for the period between the observations = the time between the observation × the square root of the product of the concentrations at the two observation times.

Example 2

A fumigation with a very high loss rate where top up gas is added to ensure that the required Ct product is achieved. Here the Ct product is calculated using equation 1. This is the type of result that can be expected from a poorly sealed fumigation under under-sheets, or a fumigation of a very sorbtive commodity where a contractual or quarantine target dose (either Ct or minimum concentration over a set time) has been specified.

Readings:

Time (hours)	Time step (hours)	Concentration (g/m^3)	Ct product ($g\ h/m^3$)	Cumulative Ct ($g\ h/m^3$)	Comments
0.0	-	-	-	-	End of gassing
2.0	2.0	20.0	†	0.0	Ct cannot be calculated
4.0	2.0	15.5	35.2	35.2	
7.0	3.0	10.0	37.3	72.5	Top up started
8.0	1.0	19.5	14.0	86.5	Top up finished
15.0	7.0	10.0	97.7	184.2	Top up started
16.0	1.0	15.5	12.4	196.6	Top up finished
24.0	8.0	4.0	63.0	259.6	
36.0	12.0	trace	*	259.6	Ct cannot be calculated
48.0	12.0	0.0	*	259.6	Ct cannot be calculated

†No contribution to Ct as gas most probably not mixed by this time and sample may not be representative of concentrations as a whole.
*Ct for this time period cannot be calculated as final value is less than a quantifiable concentration.

Example 3

A fumigation in a well sealed enclosure that has passed the pressure test and where the gas loss rate is low. Here the Ct product is calculated using equation 2. This type of fumigation is only likely to occur in an extremely well sealed enclosure with a relatively non-sorbtive commodity.

Readings:

Time (hours)	Time step (hours)	Concentration (g/m^3)	Ct product ($g\ h/m^3$)	Cumulative Ct ($g\ h/m^3$)	Comments
0.0	-	-	-	-	End of gassing
2.0	2.0	19.8	†	0.0	Ct cannot be calculated
4.0	2.0	19.7	39.5	39.5	
12.0	8.0	19.0	154.8	194.3	
24.0	12.0	18.1	222.6	416.9	
36.0	12.0	17.2	211.8	628.6	
48.0	12.0	16.4	201.6	830.2	

†No contribution to Ct as gas most probably not mixed by this time and sample may not be representative of concentrations as a whole.

Example of calculation

Using equation 2 for the period from 2 to 4 hours

$$Ct_{2,4} = \frac{(2-4) \times (19.8 + 19.7)}{2.0}$$
$$= \frac{2 \times 39.5}{2.0}$$
$$= 39.5$$

That is the Ct for the period between the observations = the time between the observation × the sum of the concentrations at the two observation times ÷ 2.0

Appendix 7

Methods for Safe Storage and Handling of Gas Cylinders

Cylinders of poisonous gases are potentially dangerous, because of their contents and because they are generally under high pressure. Fortunately, the risk of mishap can be virtually eliminated if a few simple rules are followed.

Move and store cylinders correctly

Keep Cylinder Cool: this rule should be printed on every cylinder label. Pressure will rise within the cylinder should it become heated by, for example, being located near a burner, heater, or oven, or left in full sunlight.

Store full and empty cylinders apart to avoid confusion and interruptions to fumigation procedure.

Keep cylinders upright at all times during use and transport.

Do not drop cylinders or otherwise subject them to severe physical forces.

Protect cylinders from being accidentally knocked over.

Protect cylinders stored in the open against rusting and extremes of weather. Cylinders should not be stored in conditions likely to encourage corrosion.

Take extreme care with poisonous gases

Know and understand the properties and hazards associated with each gas before using it.

Only personnel familiar with and trained in the use of poisonous gases for fumigation should be allowed to handle them. Personnel handling these gases should have available, for immediate use, canister gas masks or self-contained breathing apparatus of a design approved by the appropriate authorities. Fumigation personnel should be regularly trained in the use of this equipment.

Use gases in strict accordance with the suppliers' requirements and instructions

Make sure that suppliers' instructions are available and understood by everyone using gases during fumigations. In releasing a fumigant gas, use equipment and an application process that have been approved by the gas supplier. Follow the instructions fully; do not take shortcuts.

Read the label on the gas cylinder

Many cylinders look alike. The gas name label is the only way to tell what gas is

inside the cylinder. Do not deface the label. The use of the wrong gas could be, at best, extremely inconvenient and, at worst, disastrous.

Avoid leaks

All compressed gases (other than air) can create a hazard if they leak into the atmosphere. Even small leaks are dangerous in a confined space, as the concentration can build up over a period of time. The danger applies not only to poisonous and flammable gases, but also to gases such as carbon dioxide which is not only toxic, but also in sufficient quantity in a confined space will produce an atmosphere deficient in oxygen.

Test for leaks as follows:

- attach and tighten regulator, hose and equipment
- shut off control valve on equipment
- open cylinder valve and screw in regulator control knob to pressurise system
- close cylinder valve and watch pressure gauges
  - if pressure is retained, there is no leak in the system
  - if pressure drops, a leak is present; it should be located by going over the equipment and hoses with soapy water and a brush, and corrected.

Be prepared for emergencies

Make sure the gas supply can be turned off quickly in an emergency. Keep appropriate emergency equipment close at hand. Make sure that emergency telephone numbers—fire brigade, doctor, ambulance—are readily available.