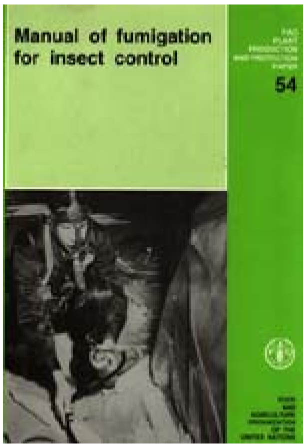

Manual of fumigation for insect control

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CONTENTS

Contents 2
Acknowledgments 5
Preface 6
Introduction 8
1. Fumigation and pest management programmes 11
2. Principles of fumigation 14
Choice of fumigant 14
Evaporation of fumigants 14
Diffusion and penetration 21
Significance of residues in foods 27
Other effects on materials 27
Dosages and concentrations 29
Toxicity of fumigants to insects 36
Acquired resistance of insects 41
3. Safety precautions and protective devices 48
Threshold limits 48
Acute and chronic hazards 49
General precautions 52
First aid training 53
Medical supervision 53
Respirators (gas masks) 55
4. Field determination of fumigants 66
Thermal conductivity analysers 66
Interference refractometers 68
Detector tubes 69
Colour indicators 69
Lamps 71
Halide meters 71
Infra-red (IR) analysers 71
Gas chromatographs 71
5. Fumigant residues 72
Nature of fumigant residues 72
Significance of fumigant residues 73
Factors affecting residue accumulation 74
Detection and analysis of residues 76
6. Chemicals used as fumigants 78
Methyl bromide 78
Phosphine 103
Hydrogen cyanide (HCN) 118
Ethylene dibromide 131
Ethylene oxide 139
Ethylene dichloride 146

Carbon disulphide 150
Carbon tetrachloride 155
Chloropicrin 158
Dichlorvos (DDVP) 162
Sulphuryl fluoride 171
Acrylonitrile 175
Minor fumigants 179
7. Fumigant mixtures 183
Acrylonitrile 184
Carbon disulphide 184
Chloropicrin 185
Ethylene dibromide 185
Ethylene dichloride 187
Methyl bromide–phosphine 188
Methyl chloroform 188
8. Space fumigation at atmospheric pressure 189
Sealing Methods and Materials 189
Fumigation Chambers 190
Fumigation under sheets 207
Fumigation of large structures 213
Mill fumigation 224
Local fumigation 225
Fumigation of bagged goods in ships and barges 227
Fumigation of empty cargo spaces 229
Railway cars and other wheeled carriers 230
Individual package fumigation 234
9. Vacuum fumigation 236
Fumigants 236
Methods 237
Equipment 238
10. Fumigation of grain in bulk 241
Methods of grain fumigation 243
Selected literature 258
11.Fumigation and controlled atmosphere storage 259
Basic requirements 259
Procedures for establishing controlled atmospheres 262
Termination of treatment 266
Safety precautions 266
Problems associated with modified atmosphere storage 266
Choice of treatment 267
Fumigation, controlled atmospheres and forced aeration 267
Selected references 268
12. Glasshouse fumigation 269
13. Plant quarantine treatments 275
14. Experimental fumigations 278

Experimental treatment ... 278
Assessment of insect mortality ... 282
Fumigation failures ... 287
Fumigation and dust explosions ... 289
15. Training in fumigation ... 290
Fumigation schedules ... 294
Guide to schedules A and B ... 295
Schedule A. Bulk fumigation of grain in upright storage ... 298
Schedule B. Bulk fumigation of grain in flat storage ... 299
Schedule C. List of plants which have sustained injury from fumigation with methyl bromide ... 300
Schedule D. Methyl bromide fumigation of actively growing plants ... 304
Schedule E. Methyl bromide fumigation of foliated dormant plants ... 305
Schedule F. Methyl bromide fumigation of nonfoliated dormant plant material ... 306
Schedule G. Methyl bromide fumigation of orchids ... 308
Schedule H. Methyl bromide fumigation of fresh fruit at atmospheric pressure ... 309
Schedule I. Methyl bromide fumigation of fresh vegetables ... 314
Schedule J. Ethylene dibromide (EDB) fumigation of fresh fruit ... 318
Schedule K. Ethylene dibromide(EDB) fumigation of fresh vegetables ... 322
Schedule L. Hydrogen cyanide (HCN) fumigation of fresh fruit and vegetables ... 323
Schedule M. Hydrogen cyanide (HCN) fumigation of dormant nursery stock ... 324
Schedule N. Fumigation of flower bulbs and corms ... 325
Schedule O. Methyl bromide fumigation of cut flowers and greenery ... 326
Schedule P. Atmospheric and vacuum fumigation for the control of pests infesting packaged plant products ... 327
Schedule Q. Fumigation of mills, empty structures and tobacco warehouses ... 339
Schedule R. Local (spot) fumigants for mills ... 341
Schedule S. Fumigation of seeds ... 343
Schedule T. Fumigation for controlling rodents and other mammalian pests, snakes, birds, snails, ants' nests, wasps and termites ... 345
Appendices ... 349
Efficient utilization of fumigation sheeting ... 349
Conversion factors and relationships useful in fumigation work ... 351
General first aid for accidents with fumigants ... 359
References ... 360

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PREFACE

This manual deals with fumigation for the control of insects above the ground. Soil fumigation is not discussed because it is a separate field of endeavour. The manual is written for the practical fumigator and for the official who is required to conduct or supervise fumigation treatments. The book may also be of interest to senior planners and consultants in crop protection who needs information on the scope and limitations of fumigation as an instrument for insect control.

Fumigation continues to play a valuable role in many pest control operations; however, both the concepts and the procedures for controlling insects and other organisms are changing. With increased public concern over the adverse effects of pesticide chemicals on human health and the environment, greater emphasis is being given to methods that can circumvent the use of these materials. Nevertheless, the need for chemical pesticides, particularly the fumigants, is likely to continue for many years to come; fumigants have unique properties and capabilities that permit use in numerous situations where other forms of control are not feasible or practical.

In bringing the subject of fumigation up to date it has been considered important to put some emphasis on the concept of pest management and the integration of pest control procedures. Fumigation should be viewed as just one of a number of techniques that can be used to prevent or control insect infestations. Best results are likely to be obtained through comprehensive management of all aspects of food storage and preservation to give maximum protection against pest infestation.

The present work is based on the manual written by H.A.U. Monro (First Edition, 1961), which gave a comprehensive account of the basic principles and practices of fumigation. Much of this information is still valid and it has been retained, largely in its original form, with new information being added where appropriate and necessary. New chapters have been added to give some information and references on other measures of control closely related to fumigation and to put the subject into perspective with a total pest control programme.

In the preparation of the manual, valuable help and guidance afforded by colleagues throughout the world is gratefully acknowledged. In addition, Jonathan Banks, Commonwealth Scientific and Industrial Research Organisation, Canberra, Australia, gave considerable assistance with the chapter on controlled atmosphere storage and Vern Walter; McAllen, Texas, US provided comments on training in fumigation. I am particularly grateful to H.V. Morley, Director of the Research Centre, Agriculture Canada, London, Ontario for valuable support and assistance in the preparation of this revision. The assistance given by the library service of Agriculture Canada and by our librarian, Dorothy Dew, is also gratefully acknowledged. T. Dumas, S.K. Hobbs, G. Lambert, F. Smeltzer and J. Witmer assisted in preparing and checking the manuscript and my daughters Judy and Eleanor provided invaluable help with the typing and final assembly of the manuscript. Photographs marked 'C British Crown Copyright' are

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INTRODUCTION

In modern terminology a fumigant is a chemical which, at a required temperature and pressure, can exist in the gaseous state in sufficient concentration to be lethal to a given pest organism. This definition implies that a fumigant acts as a gas in the strictest sense of the word.

This definition excludes aerosols, which are particulate suspensions of liquids or solids dispersed in air, and which are popularly referred to as smokes, fogs or mists. It is important to make this distinction at the outset because it emphasizes one of the most important and useful properties of fumigants: as gases they diffuse as separate molecules. This enables them to penetrate into the material being fumigated and to diffuse away afterwards. On the other hand, aerosols are unable to penetrate even a short distance into materials because their particles are deposited at the outer surfaces.

Insecticides, which are sprayed on leaves or other surfaces so that insects coming in contact with them or eating them are poisoned, sometimes exert sufficient vapour pressure to give off gas. Under certain circumstances, this gas may account for some of the toxic action - the so-called "fumigation effect". This manual will not deal with this subject; the discussion here is confined to fumigants which are dispensed so that the poison is present as gas soon after application and reaches the insect only in this form.

Present Status of Fumigation

Fumigants are still widely used for the control of insects and other pest organisms. Because of their unique characteristics and the great adaptability of the fumigation technique, fumigants can often provide effective, economical control where other forms of pest control are not feasible. In many cases treatments can be carried out on infested material without disturbing it in any way. The development of lightweight plastic sheets to enclose spaces or materials requiring fumigation has extended the use of fumigants and made control procedures easier and much more adaptable. Several modern technological developments, including instrumentation for gas detection and analysis, improved formulations as well as increased demand for effective and economical pest control measures, have done much to improve fumigation procedures.

Modern technology and research have also brought to light certain problems with fumigants that were previously unknown. Numerous investigations made on both the acute and chronic effects of fumigants have shown that some of these materials are capable of producing serious effects on human health. In some cases fumigants with excessive hazard potential have been restricted or prohibited so that they are no longer widely used for pest control in some countries.

In this edition of the manual, all of the fumigants in the previous editions are included and the nature of hazards posed by any material outlined so that the fumigator will be aware of potential problems. Fumigant use is, more and more, being determined on a risk-benefit basis, where materials with unusual hazards are used only because no effective substitute is available. When such materials are used, the fumigator should take additional precautions to avoid any hazard. Misuse or accidents that generate adverse publicity can do much harm to the practice of fumigation and may jeopardize public acceptance of other fumigants not having such effects. Great care should be taken to ensure that fumigants are always used wisely and carefully.

Fumigation Personnel

The practice of pest control is becoming increasingly specialized and requires professional personnel who are familiar, not only with the pest and the pesticide, but who also have a good knowledge of the many factors related to pest infestation and control. Even in field applications, where much of the work may be done by relatively unskilled people working under a well-trained foreman, a working knowledge of the principles of fumigation can be an asset.

In addition, reasonable physical fitness, mental alertness and the ability to understand verbal and written instructions and to carry these out carefully are required. In this field, physical fitness includes absence of any respiratory trouble which might make the operator unduly susceptible to the effects of gases or protective equipment.

Personnel assigned to fumigation work should receive thorough instructions on the properties of fumigants and training in safe methods of handling. This manual can provide the basis for a suitable course in these aspects of the subject.

Scope and Use of the Manual

The manual deals primarily with the use of fumigants as insecticides. This aspect in itself is very broad. The control of bird and mammalian pests is also mentioned in connexion with certain fumigants.

There is no discussion of soil fumigation since this is a complete subject in itself. Because control of nematodes is mainly an aspect of soil fumigation, the effect of fumigants on this group is not considered fully here.

It is not possible, or even desirable, to describe here a large number of treatments in great detail. Instead, in order to make the manual as widely useful as possible, there will be a discussion of basic principles followed by a description of some of the more general applications which can be adapted to deal with specific problems. Emphasis will be placed on those techniques which can be readily employed without the use of elaborate equipment. Expensive equipment, where it exists, is operated by personnel already thoroughly trained in the work. Some recommendations for actual treatments will be given in the various schedules, but these will be representative rather than

comprehensive. However, known exceptions and pitfalls will be stressed wherever applicable.

To avoid needless repetition, an attempt has been made to mention most subjects only once. The information required to carry out a certain technique may, therefore, have to be obtained from different chapters. For instance, if a certain fumigant is to be used in a certain type of application described in one chapter, it is essential that the section in Chapter 6 dealing with that fumigant be read to obtain additional information which may be applicable. Also, the section in Chapter 3 on precautions must be regularly consulted until a certain procedure is completely mastered.

1. FUMIGATION AND PEST MANAGEMENT PROGRAMMES

Fumigation is just one of a number of methods that can be used for controlling pests in stored products. The best control is likely to be obtained when all appropriate measures are taken to eliminate pest organisms. In an effective pest management programme, methods of prevention and control are integrated to give maximum protection of goods at the lowest possible cost. Other ways that have been found effective in preventing and controlling infestations are as follows:

1. Sanitation.
2. Exclusion of pests.
3. Low temperature - "freeze-outs", refrigeration, aeration.
4. High temperature - heating of mills.
5. Moisture control - grain drying.
6. Aeration - cooling, drying, elimination of temperature gradients.
7. Protectants - chemicals, inert dusts, natural compounds.
8. Residual or contact insecticides.
9. Atmospheric gases - carbon dioxide, nitrogen.
10. Gamma radiation, radio and sonic waves, microwaves, infra-red radiation.
11. Pheromones.
12. Insect growth regulators.
13. Insect pathogens.
14. Predators.
15. Insect resistant packaging.
16. Resistant varieties.

An effective integrated pest management system should begin with comprehensive planning to include all aspects of the problem, followed by the application of preventive and control methods. For example, the planning of pest management for a commodity like farm stored grain may be divided into five major categories:

- exclusion of the pest organism;
- inspection procedures;
- good housekeeping and sanitation;
- physical and mechanical control;
- chemical control

Infestation problems can often be reduced by careful planning so that the possibilities of pest organisms reaching the commodity will be kept to a minimum. Location of the storage relative to sources of infestation is important, as well as quality of the structure. Well-built storages, with a minimum of sites where debris can accumulate and insects develop, are desirable. Other features of the storage that should be considered include facilities for conditioning such as aeration systems or driers,

provision for proper inspection and cleaning and appropriate facilities for pest control procedures.

Preventive and control methods may include the following:

1. Use of sound structures for storage of commodities.

2. Maintaining clean conditions around storages.

3. Removal of residues of grain or other material from the storage facility four to six weeks prior to storing newly harvested produce.

4. Spraying of storage with approved residual insecticide after removal of food residues.

5. Storage of commodity in a condition suitable for optimum storage, e.g. grain is best stored at low moisture levels.

6. Treatment with appropriate insecticide protect ant at the time of storage may be desirable.

7. Use of aeration or other procedures to cool grain and maintain uniform temperature below those favourable for insect development.

8. Regular inspection to determine

(a) evidence of insect activity
(b) accumulation of moisture
(c) changes in temperature

9. If insects are detected, grain should be fumigated; where field infestation occurs grain should be fumigated within six weeks after harvest.

Fumigants are a unique and particularly valuable group of pesticides that can kill insects where no other form of control is feasible. To a large extent they are irreplaceable. The use of certain fumigants has been restricted in some countries because of suspected adverse effects. Excessive use of fumigants or the misuse of them to cause accidents and produce adverse publicity is likely to bring about even greater restrictions in their use.

By careful planning and management, fumigation may be incorporated into food preservation systems so that fumigants can be used more effectively and safely than when used independently. They should never be used as a substitute for sound management and good sanitation procedures. The benefits derived can include reduced cost of storage with improved food quality, reduced residues in food materials, greater occupational safety and less environmental contamination. All of

these benefits are of great concern to the general public and will be factors that have to be taken into consideration in the future use of fumigants.

The ultimate goal in the control of pests in stored products should be to so improve the methods of handling, storing and processing commodities, that the need for pesticides will decrease. Fumigants will then only be needed when unavoidable infestations are encountered.

2. PRINCIPLES OF FUMIGATION

CHOICE OF FUMIGANT

There are many chemical compounds which are volatile at ordinary temperatures and sufficiently toxic to fall within the definition of fumigants. In actual practice, however, most gases have been eliminated owing to unfavourable properties, the most important being chemical instability and destructive effects on materials. Damage to materials may take place in several ways, as follows:

1. Excessively corrosive compounds attack shipping containers or spoil the structure and fittings of fumigation chambers or other spaces undergoing treatment.

2. Reactive chemicals form irreversible compounds, which remain as undesirable residues in products. In foodstuffs such reactions may lead to taint or the formation of poisonous residues. Other materials may be rendered unfit by visible staining or by the production of unpleasant odours.

3. Physiologically active compounds may destroy or severely injure growing plants, fruit or vegetables, and may adversely affect seed germination.

Highly flammable compounds are not necessarily excluded if dangers of fire and explosion can be controlled by the addition of other suitable compounds, or if fumigation procedures are carefully designed to eliminate these hazards. Toxicity to human beings is not necessarily a cause for exclusion. All known fumigants are toxic to humans to a greater or lesser degree and ways can be devised for their safe handling under the required conditions of application. However, some commonly used compounds have been shown to be capable of producing long-term effects that were previously unknown. The use of such fumigants is becoming more restricted and some materials have already been eliminated from the list of fumigants approved for use in certain countries.

Table 1 lists a number of common insecticidal fumigants which have been used for many years. Although some of these fumigants may no longer be extensively used they have been included here and in other parts of the manual so that adverse effects as well as useful properties can be indicated.

The final selection of a fumigant for any particular pest control problem will be influenced by the various properties of the compound along with the type of pest organism and the nature of the commodity (Heuser, 1975). As the number of chemicals approved for use as fumigants is small, and is declining, this selection is being narrowed to a very few.

EVAPORATION OF FUMIGANTS

BOILING POINT

The boiling point of different chemical compounds generally rises with the increase of molecular weights. This generalization is borne out by the data for the fumigants shown in Figure 1, where molecular weights are plotted against boiling points. The relationship stated above holds very well, except for methyl bromide, and it demonstrates that important compounds, such as carbon tetrachloride or ethylene dibromide, will evaporate very slowly under practical fumigation conditions. If the highest possible concentrations are required at the beginning of the fumigation with such compounds, more rapid volatilization will have to be effected in some way.

Figure 1 shows that, from the physical standpoint, fumigants may be divided into two main groups according to whether they boil above or below room or moderate outdoor temperatures (20°C to 25°C). The low boiling point fumigants, such as methyl bromide, may be referred to as gaseous -type fumigants. These are kept in cylinders or cans designed to withstand the pressure exerted by the gas at the highest indoor or outdoor temperatures likely to be encountered.

The second main group of fumigants contains those with high boiling points; these are usually described as liquid-type or solid-type according to the form in which they are shipped and handled. In some kinds of work, such as grain and soil fumigation, the slow evaporation of certain liquids is an advantage because the initial flow leads to a better distribution of the gas subsequently volatilized. In other applications, where personnel have to distribute the fumigants, slow evaporation of the liquids or solids makes them safer to handle.

Included in the general term solid-type fumigants are certain materials which are not fumigants themselves, but which react to form fumigants after application. Examples are calcium cyanide powder, which reacts with atmospheric moisture to yield hydrogen cyanide (HCN), and formulations of aluminium and magnesium phosphides which also react with moisture to produce phosphine (hydrogen phosphide).

There are also some fumigants in the form of crystals and flakes that sublime to give off fumigant vapours. Examples are paradichlorobenzene and naphthalene.

MAXIMUM CONCENTRATIONS

The maximum weight of a chemical that can exist as a gas in a given space is dependent on the molecular weight of that chemical. This fact, implicit in the well-known hypothesis of Avogadro, has an important practical application. It is useless attempting to volatilize in an empty chamber more fumigant than can exist in the vapour form. Table 2 shows the maximum amounts of a number of fumigants that can be vaporized in a given space. It will be noted that the fumigants with low boiling points, such as methyl bromide or ethylene oxide, may be released in large amounts compared with high boiling point compounds, such as naphthalene and paradichlorobenzene. The data in Table 2, while useful for comparative purposes,

apply only to empty spaces. Sorption of the fumigant by the material treated in a given space will permit greater amounts to be volatilized. Nevertheless, the figures given will still apply to the amount which can exist as vapour in the free air space surrounding the fumigated material.

TABLE 1. - ESSENTIAL PROPERTIES OF FUMIGANTS IN COMMON USE FOR INSECT CONTROL

NAME AND FORMULA	MOLECULAR WEIGHT	BOILING POINT* (AT 760 MM PRESSURE) °C	SOLUBILITY IN WATER* G/100 ML	FLAMMABILITY* (BY VOLUME IN AIR) PERCENT
Acrylonitrile $CH_2 : CH.CN$	53.06	77.0	7.5 at 25°C	3-17
Carbon disulphide CS_2	76.13	46.3	0.22 at 22°C	1.25-44
Carbon tetrachloride CCl_4	153.84	77.0	0.08 at 20°C	Non-flammable
Chloropicrin $CCl_3.NO_2$	164.39	112.0	Insoluble at20°C	Non-flammable
Dichlorvos (DDVP) $CCl_2{=}CHO.Po.(OCH_3)_2$	221	120°C/14mm	Slight	Non-flammable
Ethylene dibromide $CH_2Br.CH_2Br$	187.88	131.0	0.43 at 30°C	Non-flammable
Ethylene dichloride $CH_2Cl.CH_2Cl$	98.97	83.0	**0.87 at 20°C	6-16
Ethylene oxide $CH_2.O.CH_2$	44.05	10.7	Very soluble at 20°C	3-80
Ethyl formate $H.COO\ C_2H_5$	74.05	**54.0	**11.8 at 25°C	2.7 - 13.5
Hydrogen cyanide HCN	27.03	26.0	Very soluble at 20°C	6-41
Methyl bromide CH_3Br	94.95	3.6	1.3 at 25°C	Non-flammable
Methyl formate $H.COO\ CH_3$	60.03	**31.0	**30.4	5.9 - 20
Paradichlorobenzene $C_2H_4Cl_2$	147.01	173.0	0.008 at 25°C	(Flash point***
Phosphine PH_3	34.04	**-87.4	**Very slightly soluble	1.79
Sulphuryl fluoride SO_2F_2	102.6	-55.2	Slight	Non-flammable
Trichloroethylene $CHCl : CCl_2$	131.4	86.7	**Insoluble	Non-flammable

* Unless other reference given, boiling point and solubility data are from Martin (1961) and flammable limits from Coward and Jones (1952).
** From Handbook of chemistry and physics, 38th edition 1956/57, Chemical Rubber

Publishing Co., Cleveland, Ohio, U.S.A.
***3 Sax (1951).

Commodities treated and remarks

Tobacco and plant products; also spot treatment. Injures growing plants, fresh fruit and vegetables. Marketed with carbon tetrachloride.

Grain. Usually as ingredient of non-flammable mixtures.

Only weakly insecticidal. Used chiefly in mixture with flammable compounds in grain fumigation to reduce fire hazard and aid distribution.

Grains and plant products. Injurious to living plants, fruit and vegetables. Highly irritating lachrymator. Bactericidal and fungicidal.

Insects in open space of structures. Does not penetrate commodities.

General fumigant. Particularly useful for certain fruit; may injure growing plants.

Seeds and grains. Usually mixed with carbon tetrachloride.

Grains, cereals and certain plant products. Toxic at practical concentrations to many bacteria, fungi and viruses. Strongly phytotoxic and affects seed germination.

Application to individual packages of dried fruit.

General fumigant, but may be phytotoxic. Safe on seeds but not recommended for fresh fruit and vegetables.

General fumigant. May be used with caution for nursery stock, growing plants, some fruit and seeds of low moisture content.

Usually mixed with CO2. Formerly used for grain, now mainly for stored furs.

Control borers in peach trees and soil insects. Applied as crystals. May affect seed germination.

Grain and processed food fumigant; gas generated from aluminium or magnesium phosphide.

Control of dry-wood termites in structures.

Non-flammable ingredient of grain fumigants. Sometimes used alone.

FIGURE 1. - Relationship between molecular weight and boiling point of some fumigants.

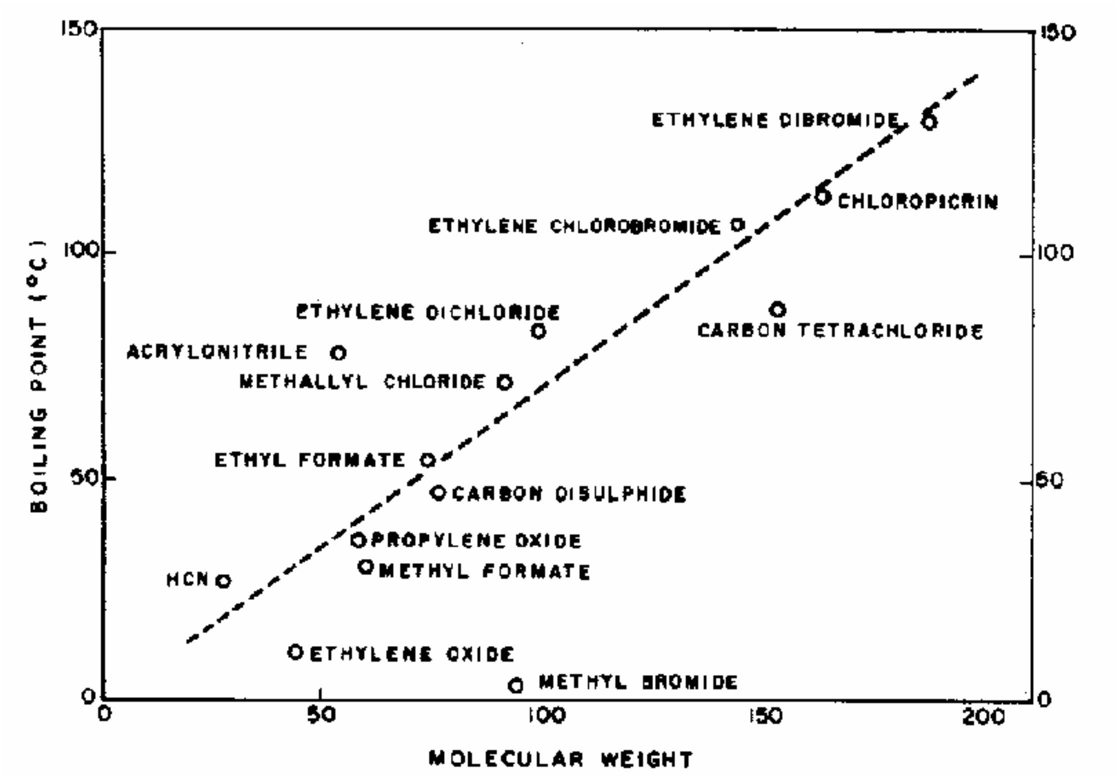


TABLE 2. – MAXIMUM WEIGHTS OF VARIOUS FUMIGANTS WHICH CAN EXIST IN VAPOUR FORM IN AN EMPTY FUMIGATION SPACE AT DIFFERENT TEMPERATURES[1]

FUMIGANT	MAXIMUM WEIGHT, IN GRAMMES/CUBIC METRE[2] AT INDICATED TEMPERATURES							
	0°C	5°C	10°C	15°C	20°C	25°C	30°C	35°C
	(32°F)	(41°F)	(50°F)	(59°F)	(68°F)	(77°F)	(86°F)	(95°F)
Acrylonitrile	102.6	129.8	164.4	206.3	252.9	319.1	397.8	482.4
Carbon disulphide	568.1	701.1	843.7	1010.9	1297.2	1430.8	1740.9	2 096.3
Carbon tetrachloride .	288.5	363.0	460.9	572.6	730.9	916.8	1145.4	1 398.5
Chloropicrin	57.8	79.5	108.7	139.5	179.5	220.6	277.8	358.7
Dichlorvos (DDVP)	0.02	0.03	0.05	0.08	0.13	0.21	0.32	0.48
Ethylene dibromide	38.5	54.1	63.7	83.5	112.8	141.2	173.6	214.7
Ethylene dichloride	133.4	173.7	223.7	282.0	350.1	430.3	537.1	668.2
Ethylene oxide	1331.5	1606.6	1854.5	1862.4	1830.4	1800.0	1771.2	1 740.8
Hydrogen cyanide	418.7	532.0	643.4	751.3	900.4	1072.2	1084.7	1 067.7
Methyl bromide	3839.3	4152.8	4079.4	4008.6	3940.2	3874.1	3810.1	3 748.3
Naphthalene	0.15	0.22	0.33	0.43	0.56	0.69	0.95	1.40
Paradichlorobenzene	0.69	1.61	2.49	3.18	5.14	7.89	11.64	17.56
Phosphine	1514.4	1487.2	1460.9	1435.5	1411.0	1387.4	1364.5	1 342.3
Sulphuryl fluoride	4546.0	4464.2	4385.3	4309.2	4235.7	4164.6	4095.9	4 029.4
Carbon dioxide	1959.8	1924.6	1890.6	1857.8	1826.1	1795.4	1765.8	1737.1

[1]Values calculated from formulas derived by Roark and Nelson (1929).–[2]Equivalent to milligrams per litre, or ounces(avoirdupois)per 1000 cubic feet.

LATENT HEAT OF VAPORIZATION

Unless it is sustained by warming from an outside source, the temperature of an evaporating liquid constantly drops owing to the fall in energy caused by the escape of molecules with greater than average energy. Thus, evaporation takes place at the expense of the total heat energy of the liquid. The number of calories lost in the formation of one gram of vapour is called the latent heat of vaporization of the liquid. Some fumigants have higher latent heats than others.

Both HEN and ethylene oxide, with latent heats of 210 and 139 respectively, absorb considerably more heat in passing from liquid to than do methyl bromide and ethylene dibromide, with latent heats of 61 and 46 respectively.

The factor of latent heat is of important practical significance. The high pressure fumigants, such as HCN, ethylene oxide and methyl bromide, are usually kept under pressure in suitable cylinders or cans. On release into the atmosphere, volatilization takes place rapidly and, unless the lost heat is restored, the temperature of the fumigant may fall below the boiling point and gas may cease to be evolved. Also, as the liquid changing to gas is led through metal pipes and tubes, or rubber tubing, the fall in temperature may freeze the fumigant in the lines and prevent its further passage. In many applications, to be described elsewhere in this manual, it is advisable to apply heat to the fumigant as it passes from the container into the fumigation space.

Fumigants that are liquids at normal temperatures and are volatilized from evaporating pans or vaporizing nozzles may require a source of heat, such as a hot plate, in order that full concentrations may be achieved rapidly.

DIFFUSION AND PENETRATION

As stated above, fumigants are used because they can form insecticidal concentrations: (a) within open structures or (b) inside commodities and in cracks and crevices into which other insecticides penetrate with difficulty or not at all. Hence, it is necessary to study the factors that influence the diffusion of gases in every part of a fumigation system. This study includes the behaviour of fumigants both in empty spaces and also in structures loaded with materials into which the gas is required to penetrate.

LAW OF DIFFUSION

Graham's law of diffusion of gases states that the velocity of diffusion of a gas is inversely proportional to the square root of its density.

Also, the densities of gases are proportional to their molecular weights. Therefore, a heavier gas, such as ethylene dibromide, will diffuse more slowly throughout an open space than a lighter one such as ethylene oxide. While this basic law is of importance, especially for empty space fumigations, the movement of gases in contact with any internal surface of the structure or within any contained materials is greatly modified by the factor of sorption discussed below.

The rate of diffusion is also directly related to temperature, so that a given gas will diffuse more quickly in hot air than in cold air.

SPECIFIC GRAVITY AND DISTRIBUTION

Many of the commonly used fumigants are heavier than air. A notable exception is hydrogen cyanide. If a gas heavier than air is introduced into a chamber filled with air and it is not agitated by fans or other means, it will sink to the bottom and form a layer below the air. The rate of mixing between the two layers may be very slow. For example, in a fumigation of the empty hold of a ship with the heavy gas methyl bromide where the fumigator had neglected to place a circulating fan, a sharp demarcation was observed between the lower half with the gas, where all of the insects were killed, and the upper part, where complete survival occurred (Monro et al, 1952).

In good fumigation practice, settling or stratification will not be encountered if adequate provision is made to disperse the gas properly from the very beginning of the treatment. Even distribution can be ensured by employing singly or in suitable combination: multiple gas inlets, fans or blowers and/or circulation by means of ducts and pipes. Contrary to popular belief, once a gas or number of gases heavier than air have been thoroughly mixed with the air in a space, settling out or stratification of the heavier components takes place very slowly; so slowly, in fact, that once a proper mixture with air has been secured, the problem of stratification of a heavier than-air fumigant is of no practical importance for the exposure periods commonly used in fumigation work.

MECHANICAL AIDS TO DIFFUSION

It has already been suggested that distribution and penetration can be aided and hastened by the use of blowers and fans. Such propellers may work free in the structure or through a system of circulating ducts. These devices may also add greatly to the efficiency of the fumigation process by hastening the volatilization of high boiling point liquids from evaporating pans and by preventing stratification of heavy gases. Also, a factor known as the Turtle effect* has proved useful in the fumigation of certain materials susceptible to injury. It was shown that rapid stirring by a centrifugal fan in a fumigation chamber at atmospheric pressure greatly hastened the attainment of uniform concentrations of methyl bromide in all parts of a load of early potatoes, so that the consignment was not overdosed at the outside of the packages or under dosed at the centre (Lubatti and Bunday, 1958). In a four-hour exposure period, rapid stirring for one hour at the beginning of the treatment was, to all intents and purposes, as effective as continuous stirring for the whole time.

Circulating devices suitable for particular purposes will be discussed in more detail in the section of this manual dealing with specific practices.

SORPTION

A very important factor affecting the action of fumigants is the phenomenon known as sorption. It is not possible in this manual to give a complete explanation of sorption, because the interaction of all forces involved is complex. Fortunately, for the purpose of understanding fumigation practice, it is possible to give a general account of the important factors concerned.

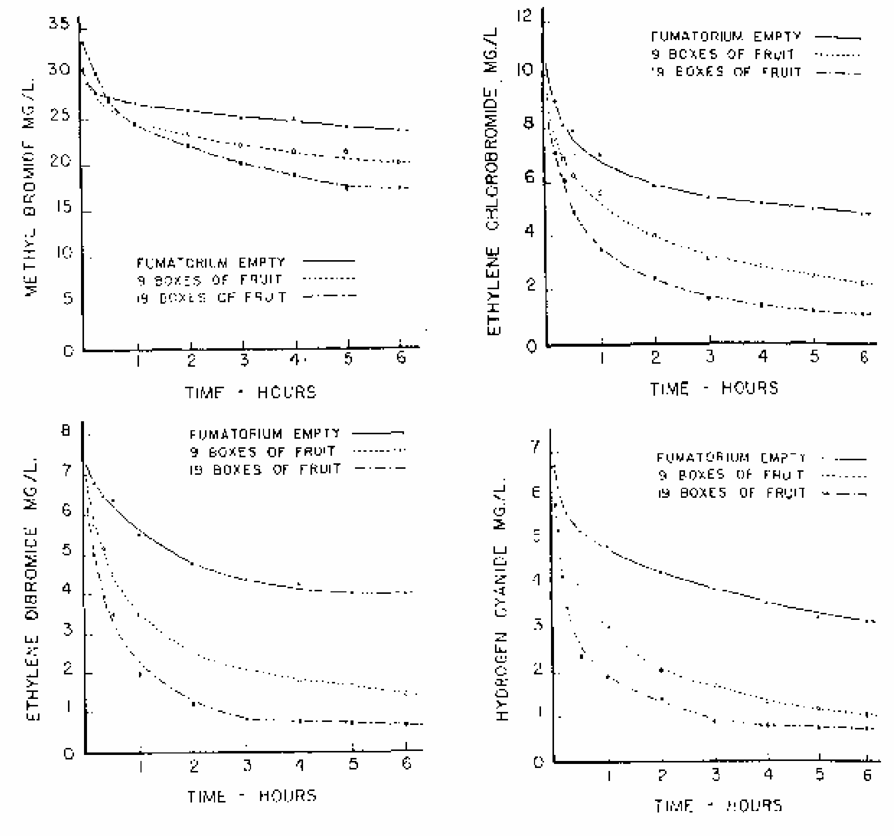
In the relationship of gases to solids, sorption is the term used to describe the total uptake of gas resulting from the attraction and retention of the molecules by any solid material present in the system. Such action removes some of the molecules of the gas from the free space so that they are no longer able to diffuse freely throughout the system or to penetrate further into the interstices of the material. In fumigation practices, collision with air molecules tends to slow down gaseous diffusion through the material and sorption takes place gradually. Thus, there is a progressive rather than immediate lowering of the concentrations of the gas in the free space. This gradual fall in concentration is illustrated in the graphs in Figure 2. The curves for each of the four compounds clearly show the differences in degree of sorption of the fumigants by the same load in the chamber. Throughout the exposure period of six hours, the fall in concentration of methyl bromide was proportionately less compared with that for the three other fumigants, both in the empty chamber and with the two loads of oranges. This was due to the fact that the internal surface of the chambers and the boxes of oranges both sorbed less of the methyl bromide than of the other gases in proportion to the applied dosage. Sorption under a given set of conditions determines the dosage to be applied, because the amount of fumigant used must be sufficient both to satisfy the total sorption during treatment and also to leave enough free gas to kill the pest organisms.

The general term sorption covers the phenomena of adsorption and absorption. These two are reversible because the forces involved, often referred to as van der Waal's forces, are weak. On the other hand, a stronger bonding called chemisorption usually results in chemical reaction between the gas and the material and is irreversible under ordinary circumstances (Berck, 1964).

Physical Sorption

From the point of view of practical fumigation, adsorption and absorption, being both physical in nature and reversible, may be discussed in this manual under the heading of physical sorption. However, it is necessary to make some distinction between them at the outset because the forces involved may be less with adsorption than with absorption.

FIGURE 2. - Relationship between load (boxes of oranges) and concentration of fumigant in gas phase in a 3-cubic-metre chamber at atmospheric pressure and 21°C (Sinclair and Lindgren, 1958).



Stated briefly, adsorption is said to occur when molecules of a gas remain attached to the surface of a material. Because some absorbents, such as charcoal or bone meal, are highly porous bodies with large internal surfaces, adsorption may also occur inside a given body.

Absorption occurs when the gas enters the solid or liquid phase and is held by capillary forces that govern the properties of solutions. For instance, a gas may be absorbed in the aqueous phase of grain or in the lipid phase of nuts, cheese or other fatty foods (Berck, 1964).

Physical sorption, considered generally, is an extremely important Factor affecting the successful outcome of fumigations. Apart from specific reactions between certain gases and commodities, it may be stated as a general rule that those fumigants with higher boiling points tend to be more highly sorbed than the more volatile compounds. This is illustrated in the graphs in Figure 2; with this particular load there is greater sorption of ethylene dibromide (boiling point 131°C) and of hydrogen cyanide (boiling point 26°C) than of methyl bromide (boiling point 3.6°C). (The considerable difference in the sorption of hydrogen cyanide and methyl bromide is due to factors other than boiling point or molecular weight.)

Physical sorption varies inversely as the temperature, and is thus greater at lower temperatures. This fact has important practical applications. It is one of the reasons why dosages have to be progressively increased as the temperature of fumigation is lowered (Figure 3).

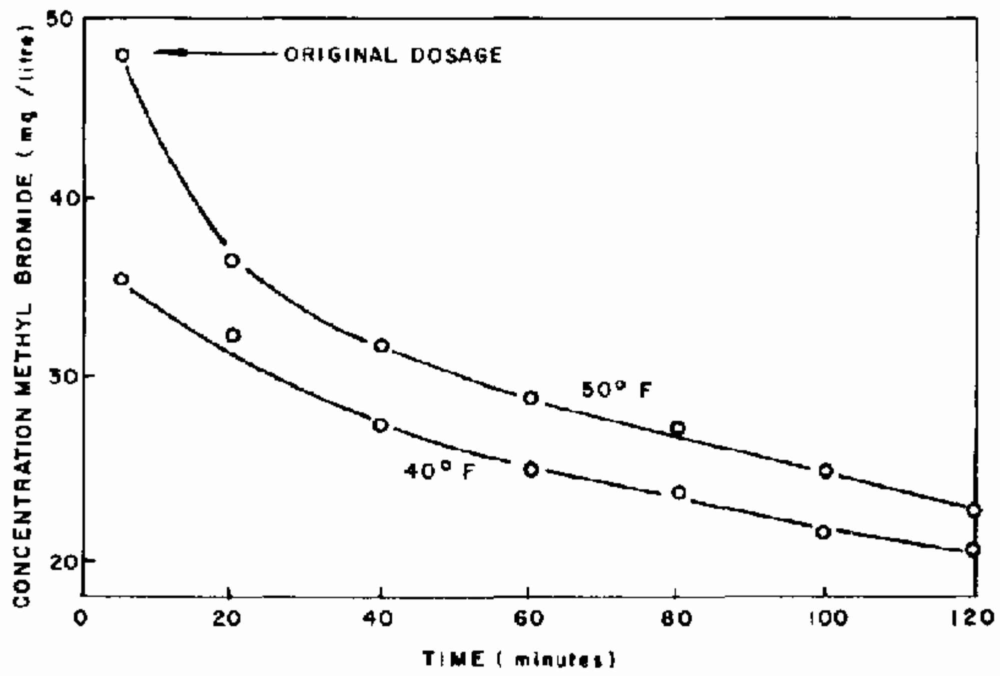
Sorption may also be influenced by the moisture content of the commodity being fumigated. This was demonstrated by Lindgren and Vincent (1962) in the fumigation of a number of foodstuffs with methyl bromide; at higher moisture contents more fumigant was sorbed. This effect may be important with fumigants which are soluble in water to any significant degree.

The specific physical reaction between a given gas and a given commodity cannot be accurately predicted from known laws and generalizations. Usually, a certain fumigant must be tested with each material concerned before a recommendation for treatment can be drawn up.

Desorption

When a treatment is completed and the system is ventilated to remove the fumigant from the space and the material, the fumigant slowly diffuses from the material. This process is called Resorption and is the reverse of physical sorption. With the common fumigants and the commodities usually treated, residual vapours are completely dissipated within reasonable periods, although the length of time varies considerably according to the gas used and the material treated. Because of the inverse effect of temperature, dissipation of the fumigant usually takes place more slowly when the material is cold and may be hastened by warming the space and its contents.

FIGURE 3. – Effect of temperature on sorption of fumigant by identical loads (weights) of peaches. The same dosage of 48 g per m of methyl bromide was applied in each treatment. (Dumas and Monro, 1966)



Humidity also facilitates desorption of fumigants; at high humidity, wheat fumigated with ethylene dibromide was found to desorb 80 percent more of the fumigant than at very low humidity (Dumas and Bond, 1979). As humidity's can change appreciably with changing temperature, the rate of desorption may be dependent on the combined effect of both factors.

Removal of desorbing gas can be speeded up by employing fans and blowers to force fresh air through the material. Natural ventilation may be hastened by taking the goods out of doors where advantage can be taken of wind, thermal air currents and the warming effect of sunlight.

Some of the residual fumigant, usually small in quantity, may not be desorbed because of chemical reaction with the material.

CHEMICAL REACTION

If chemical reaction takes place between the gas and the material, new compounds are formed. This reaction is usually characterized by specificity and irreversibility. If the reaction is irreversible, permanent residues are formed. Examples are the reaction between hydrogen cyanide (HCN) and the reducing sugars in dried fruits with the formation of cyanohydrins (Page and Blackith, 1956) or the appearance of inorganic bromide compounds after treatment of some foodstuffs with methyl bromide (McLaine and Monro, 1937).

Because this type of reaction is essentially chemical it may be expected that its intensity varies directly with the temperature. This assumption has been confirmed by observation. Dumas (1973) has reported proportionately less fixed bromide residues in fruits as the temperature of fumigation was reduced from 25 to 4°C. Lindgren et al (1962) found an increase in the bromide content of wheat as the temperature during fumigation rose from 10 to 32°C.

SIGNIFICANCE OF RESIDUES IN FOODS

RESIDUE TOLERANCES

In recent years attention has been focussed on the nature and possible effects on human beings of insecticidal residues appearing in foodstuffs. World-wide interest in this problem is reflected in the fact that international organizations such as the Food and Agriculture Organization of the United Nations (FAO) and the World Health Organization (WHO) have set up special committees to investigate and report on the nature and significance of residues formed in foodstuffs as the result of the application of pesticides at different stages (as seed dressings, during growth, storage, transportation, etc.) prior to human consumption. These special committees review a number of pertinent factors involved in the use of each pesticide. Important factors, among others, are the toxicological significance of any residues formed and the average fraction of the total diet likely to be constituted by a food containing this residue. Through their Codex Alimentarius Committee these organizations undertake "to recommend international tolerances for pesticide residues in specific food products."

Such recommendations are not binding on Member Nations of these organizations but are intended to be used as guides when particular countries are formulating their own regulations for pesticide residue tolerances.

Fumigants may form residues when used on foodstuffs for insect control. In this manual the nature and significance of residues formed are discussed in Chapter 5 and under the heading of each particular fumigant in Chapter 6. No attempt has been made to list tolerances established by individual countries as these are altered from time to time. For current information it is necessary to consult the official publications on this subject.

A comprehensive review of fumigant residues has been given by Lindgren et al (1968).

OTHER EFFECTS ON MATERIALS

Apart from the question of significant residues in foodstuffs, there is the problem of other effects which have a direct bearing either on the choice of the particular fumigant or on the decision as to whether fumigation is possible at all. The main types of reaction may be summarised as follows:

PHYSIOLOGICAL EFFECTS

1. Nursery Stock and Living Plants

(a) Stimulation of growth

(b) Retardation of growth

(c) Temporary injury and subsequent recovery

(d) Permanent injury, usually followed by death

2. Seeds

(a) Stimulation of germination

(b) Impairment or total loss of germination

(c) Poor growth of seedlings from germinated seeds

3. Fruit and Vegetables

(a) Visible lesions

(b) Internal injury

(c) Shortening of storage life

(d) Delay of ripening

(e) Stimulation of storage disorders

4. Infesting Organisms

(a) Death

(b) Stimulation of growth or metamorphosis

(c) Delay in development

(d) Stimulation of symptoms of disease (so-called "diagnostic effect")

PHYSICAL AND CHEMICAL EFFECTS ON NONLIVING MATERIALS

1. Production of foul or unpleasant odours in furnishings or materials stored in premises.

2. Chemical effects that spoil certain products (for example, some fumigants render photographic films and papers unusable).

3. Reaction with lubricants followed by stoppage of machinery (clocks will often stop after fumigation with HCN).

4. Corrosive effects on metals (phosphine reacts with copper, particularly in humid conditions).

DOSAGES AND CONCENTRATIONS

There should be a clear understanding of the difference between dosage and concentration.

The dosage is the amount of fumigant applied and is usually expressed as weight of the chemical per volume of space treated. In grain treatments, liquid-type fumigants are often used and the dosage may be expressed as volume of liquid (litres or gallons) to a given volume (amount of grain given as litres or bushels) or sometimes to a given weight (quintals, metric tonnes or tons).

From the moment that a given dosage enters the structure being fumigated, molecules of gas are progressively lost from the free space either by the process of sorption and solution described above or by actual leakage from the system, if this occurs. The concentration is the actual amount of fumigant present in the air space in any selected part of the fumigation system at any given time. The concentration is usually determined by taking samples from required points and analysing them. It may thus be said that the dosage is always known because it is a pre-determined quantity. Concentration has to be determined because it varies in time and position according to the many modifying factors encountered in fumigation work.

Three methods of expressing gas concentrations in air are in common use: weight per volume, parts by volume and percent by volume.

WEIGHT PER VOLUME

For practical designation of dosages, this is the most convenient method because both factors - the weight of the fumigant and the volume of the space - can be easily determined. In countries using the metric system, this is usually expressed in grams per cubic metre (g/m^3), whereas in countries using the British system of weights and measures, expression is usually in terms of pounds or ounces avoirdupois (avdp) per 1 000 cubic feet ($lb/1\ 000\ ft^3$ or oz/1 000ft).

By a fortunate coincidence in units of measurement, grams per cubic metro are, for all practical purposes, equal to ounces per thousand cubic feet. Thus, recommended dosages can readily be converted from one system to the other*. Conversion factors for the various units are given in Appendix 2.

In reports of laboratory experiments, dosages and concentrations are usually given in milligrams per litre (mg/l), equivalent to grams per cubic metre.

PARTS OR PERCENT BY VOLUME

Parts by volume and percent by volume will be discussed together because both modes of expression give the relative numbers of molecules of gas present in a given volume of air. The values for both modes have the same digits, but the decimal points are in

different places (3 475 parts per million by volume of a gas is the same as 0.3475 percent by volume).

Parts per million of gases in air are used in human and mammalian toxicology and in applied industrial hygiene. Percent by volume is used in expressing the flammability and explosive limits of gases in air.

CALCULATIONS FOR CONVERSION OF CONCENTRATION VALUES

By means of simple calculations giving useful approximations, values may be converted from weight per volume to parts by volume and vice versa. These calculations take into account the molecular weight of the gas and the fact that, with all gases, the gram molecular weight of the substance occupies 22.414 litres at 0°C and 760 millimetres pressure. (If precise values are needed for the other temperatures and pressures, corrections for absolute temperature and pressure may be made in the usual manner.)

A. To convert grams per cubic metre (or milligrams per litre or ounces per 1 000 cubic feet) into parts by volume.

1. Divide the given value by the molecular weight of the gas and multiply by 22.4; the resulting figure is the number of cubic centimetres (cm) of gas per litre of air.

2. One thousand times the figure obtained is the value in parts per million by volume.

3. One tenth of the figure obtained in (1) is the percentage by volume.

Example. TO CONVERT 1G/M³ OF PH3 (MOLECULAR WEIGHT 34 APPROXIMATELY)

(1x22.4)/34	= .659 cm^3 per litre = 659 parts per million by volume approximately = .0659% by volume approximately

B. To convert parts per million (or percentage of volume) of gases to grams per cubic metre (or milligrams per litre or ounces per 1 000 cubic feet):

1. Divide the parts per million by 1 000, or multiply the percentage by ten to give the number of cubic centimetres of gas per litre of air.

2. Multiply this figure by the molecular weight of the gas in question and divide by 22.4.

Example.
TO CONVERT 400 PPM OF METHYL BROMIDE (MOLECULAR WEIGHT 94.95 = 95 APPROXIMATELY)

400 ppm	= 0.04% of volume = 0.4cm(3) per litre = (0.4 x 95)/22.4 = 1.7g/m^3 (or mg/l or oz per 1 000 ft^3)

Comparative figures for weights and volumes at various levels have been calculated for the important gases, and these are given in the tables accompanying the subsequent discussion of each particular gas.

CONCENTRATION X TIME (c x t) PRODUCTS

Most fumigation treatments are recommended on the basis of a dosage given as the weight of chemical required for a certain space - expressed as grams per cubic metre or pounds per 1 000 cubic feet or as volume of liquid applied to a certain weight of material - expressed as litres per quintet or gallons per 1 000 bushels. Usually, this designation of dosage is followed by a statement of the length of the treatment in hours and the temperature or range of temperature at which the schedule will apply. While such recommendations are usually based on treatments that have proved successful under certain conditions, they should also take into account the fact that certain factors may modify the concentrations left free to act against the insects. One important factor already mentioned is the effect of loads of different sizes (Figure 2). Another is the leakage from the structure undergoing treatment. What is really important is the amount of gas acting on the insects over a certain period of time. For instance, it is known (Bond and Monro, 1961) that in order to kill 99 percent of larvae of Tenebroides mauritanicus (L.) at 20°C, a concentration of 33.2 milligrams per litre of methyl bromide must be maintained for 5 hours. The product 33.2 milligrams per litre x 5 hours = 166 milligrams per litre x hours is known as the concentration x time product needed to obtain 99 percent control of this insect (Figure 4). It can be abbreviated and referred to as the c x t product. In the literature it is often expressed numerically with the notation mg h/l (milligram hours per litre) In this example it would be known as the lethal dose for 99 percent of the population, or the LD(99).

In order to apply this method of treatment designation to practical fumigations, it is necessary to make reasonably correct determinations of the fumigant concentrations required to kill the insects under certain specific conditions; important modifying conditions are temperature and humidity. One such determination is illustrated graphically in Figure 4. Note that in this figure the concentration curve tends to flatten out for short exposures at high concentrations and long exposures at low concentrations and at these extremes, which are not likely to be employed in practice, the constant value for the c x t product does not hold. To illustrate specifically the use

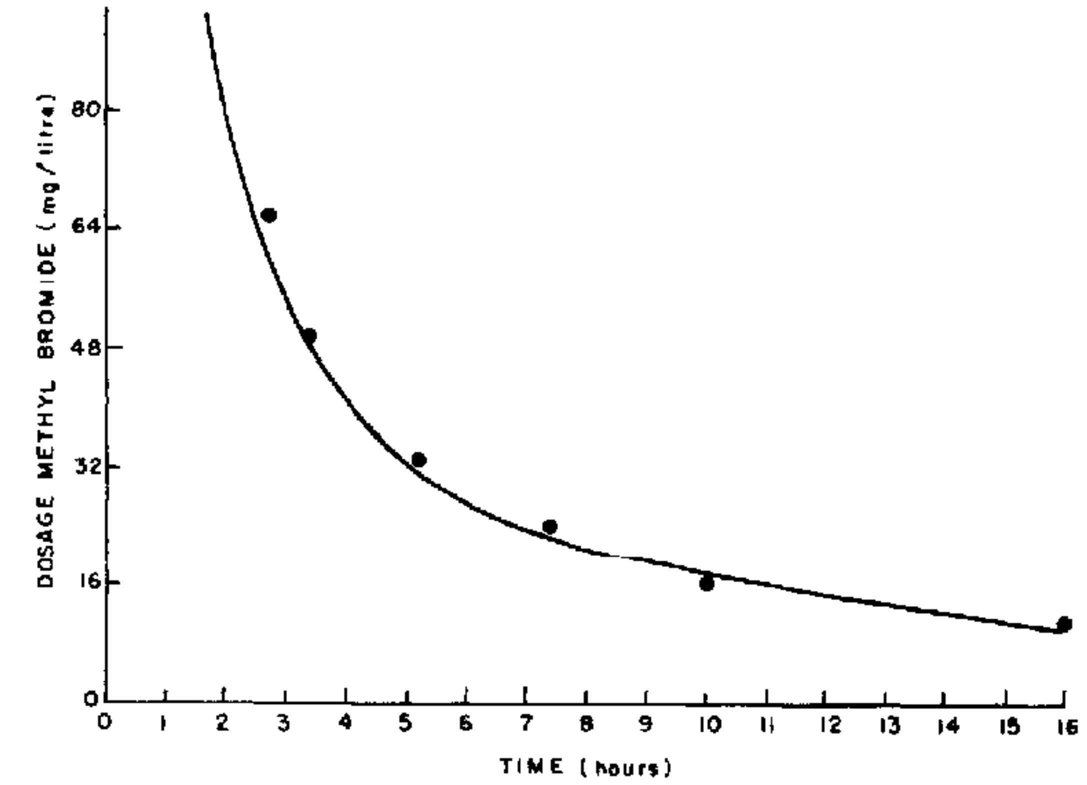
of the data in Figure 4, Table 3 sets out the required concentration x time products to bring about 99 percent mortality of mauritanicus using methyl bromide at 20°C and 70 percent relative humidity for various exposures:

TABLE 3. – REQUIRED CONCENTRATION X TIME (C X T) PRODUCTS TO OBTAIN 99 PERCENT MORTALITY OF TENEBROLDES MAURITANICUS

CONCENTRATION METHYL BROMIDE	EXPOSURE	C X T PRODUCT
MG/L	HOURS	MG H/L
83	2	166
55.3	3	166
41.5	4	166
33.2	5	166
23.7	7	166
16.6	10	166

It must be emphasized again that before they are applied in practical use each product must be calculated for the different stages of an insect species at a certain temperature and humidity. Under practical conditions, variations in temperature are particularly important. In practice, several insect species or stages of a given insect may be treated and therefore the c x t product required is that which is effective against the most tolerant species or stage present in the system.

FIGURE 4. – Insect mortality and concentration x time products. A curve showing the relationship between concentration of methyl bromide and time of exposure against fourth instar larvae of Tenebroides mauritanicus for 99 percent mortality at 20°C.(Bond and Monro, 1961)



The value and possible application of the c x t product for the fumigation of insects has been investigated by a number of workers (see particularly Whitney and Walkden, 1961; Harein and Krause, 1964; Estes, 1965; Bell and Glanville, 1973; Bell, 1977a, 1978). The important modifying effects of temperature, humidity and the moisture content of the commodity are emphasized. Kenaga (1961) described the use of graphs to estimate the effective use of c x t products of eight different fumigants against Tribolium confusum Duv. under varying conditions of time and temperature. Heseltine and Royce (1960) showed how integrated c x t products of ethylene oxide and methyl bromide may be used in practice with the aid of specifically designed concentration indicators in the form of sachets.

The use of integrated c x t products is particularly useful in routine fumigations when the reaction of a particular species or groups of species has been carefully worked out under the range of conditions likely to be encountered. It has been used successfully in large-scale eradication campaigns (Armitage, 1955; Monro, 1958c).

Figure 5 and Table 4 show how an integrated c x t product of methyl bromide may be applied in dealing with a specific problem. In this instance a hypothetical situation is illustrated in simplified form to show how the method could be applied under more complex conditions with multiple gas sampling points. The target of the fumigation is an insect which requires for complete control, under the prevailing conditions of temperature and humidity, a c x t product of 190 gram hours per cubic metre (9 h/m), which is equivalent to 190 milligram hours per litre (mg h/l).

Leakage from the 100 m³ structure and sorption by the commodity are two factors that in this instance influence the concentration of fumigant in the free space and thus within the commodity It is known that an initial dosage of 32 grams per cubic metre (g/m) may bring about the desired conditions for this load of commodity in a 12-hour exposure period if the concentration in the free space is maintained above 20 milligrams per litre (mg/l) during the entire exposure. This nominal dose is introduced and concentration readings are made at regular intervals using a thermal conductivity analyser (see Chapter 4). Samples are taken from points in the free space and at the centre of the commodity then the data are plotted on a graph as shown in Fig. 5. At the beginning, particular attention is paid to the free space readings. After 2.5 hours it is clear that the free space concentration will fall below the stipulated 20 mg/l and 0.5 kg of fumigant are added to the system. Again, after a further 2.5 hours (total elapsed time 5 hours) another 0.5 kg is added to sustain the concentration. After 11.7 hours the desired c x t product of 190 9 h/m³ has been attained and the treatment is terminated by initiating aeration. The integrated c x t product obtained within the commodity, calculated from the concentration plot, is arrived at as shown in Table 4.

Recommendations based on the c x t product principle provide a sound means of ensuring that the treatment is adequate to control the insects.

FIGURE 5. - Chart of progress of a fumigation with methyl bromide designed to achieve a cumulative c x t product of 190 9 h/m3.

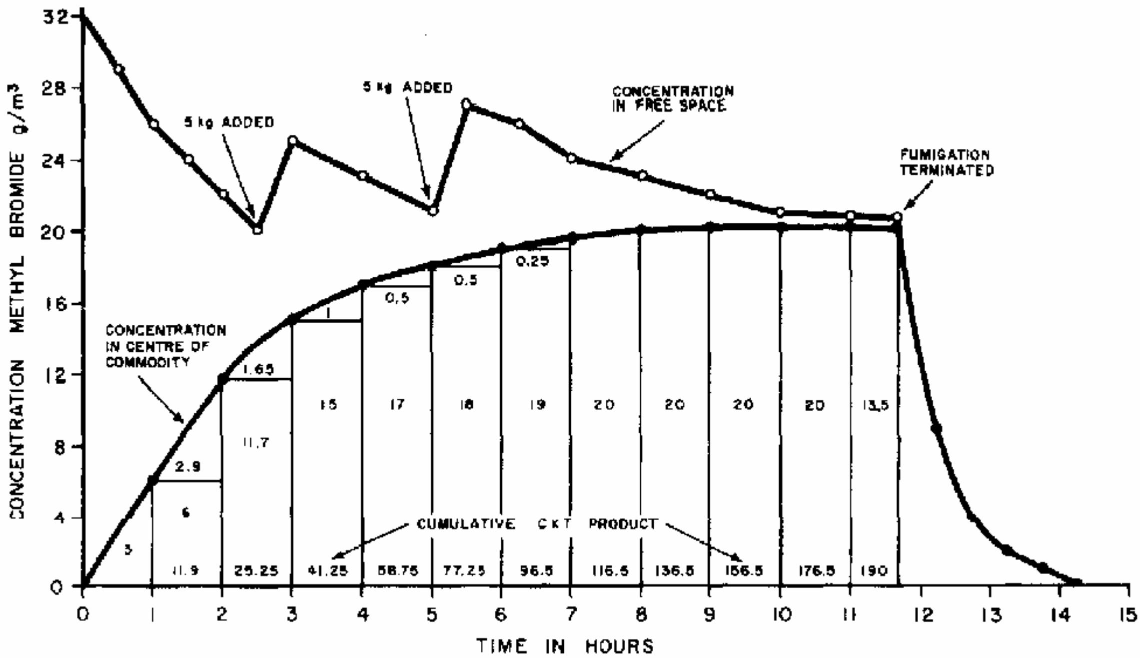


TABLE 4. - INTEGRATED CONCENTRATION X TIME PRODUCTS WITHIN THE INFESTED COMMODITY

HOURS	RECTANGLE	TRIANGLE	TOTAL AREA	CUMULATIVE
MG H/L				
1		3	3	3
2	6	2.9	8.9	11.9
3	11.7	1.65	13.35	25.25
4	15	1	16	41.25
5	17	0.5	17.5	58.75
6	18	0.5	18.5	77.25
7	19	0.25	19.25	96.5
8	20	-	20	116.5
9	20	-	20	136.5
10	20	-	20	156.5
11	20	-	20	176.5
11.7	13.5	-	13.5	190.0

Dosage schedules are, perhaps, best given in terms of weight of chemical required for a certain space for a specified period of time along with the c x t products necessary to achieve control. Thus by monitoring gas concentrations during treatment, an applicator can add gas, extend the exposure or make other changes necessary to ensure success. For plant quarantine work, recommendations based on the c x t principle are particularly valuable because they promote uniformity in standards and permit reliable certification of goods so treated. Schedules based on these concepts are in use in several countries, e.g. Plant Protection and Quarantine Treatment Manual (USDA, 1976). For other treatments of stored products, where sorption in the commodity is appreciable, schedules based on the c x t principle but given in terms of weight of fumigant per unit volume of space and per unit weight of goods for specified exposure times have been worked out for some commodities (Thompson, 1970).

While the c x t method is useful for most fumigants, it cannot be employed with phosphine. Although concentration and exposure time are still the main factors that determine toxicity of this fumigant, the length of the exposure time is of great importance. Phosphine is a slow acting poison that is absorbed slowly by some insects even at high concentrations (Bond et al, 1969). Therefore, high concentrations may not increase toxicity; in fact, they may cause insects to go into a protective narcosis, as described later in this chapter. In a phosphine fumigation certain minimum concentrations are required, and therefore gas analysis should be carried out to ensure the presence of sufficient gas. For most treatments the manufacturers' directions will

provide adequate treatment if no excessive loss through leakage or sorption occurs and adequate periods are allowed under gas.

TOXICITY OF FUMIGANTS TO INSECTS

As far as is known at present, fumigants enter the insect mainly by way of the respiratory system. The entrance to this system in larvae, pupae and adults is through the spiracles, which are situated on the lateral surfaces of the body. The opening and closing of the spiracles are under muscular control. To enter insect eggs, gases diffuse through the shell (chorion) of the egg or through specialized "respiratory channels". It has been shown that some gases may diffuse through the integument of insects, but at present the comparative importance of this route for the entry of fumigants is not known.

It is known that the poisoning of an insect by a fumigant is influenced by the rate of respiration of that insect; any factor that increases the rate of respiration tends to make the insect more susceptible.

The practical significance of the more important factors influencing the toxic action of fumigants is discussed in the following paragraphs.

EFFECT OF TEMPERATURE

General Effects

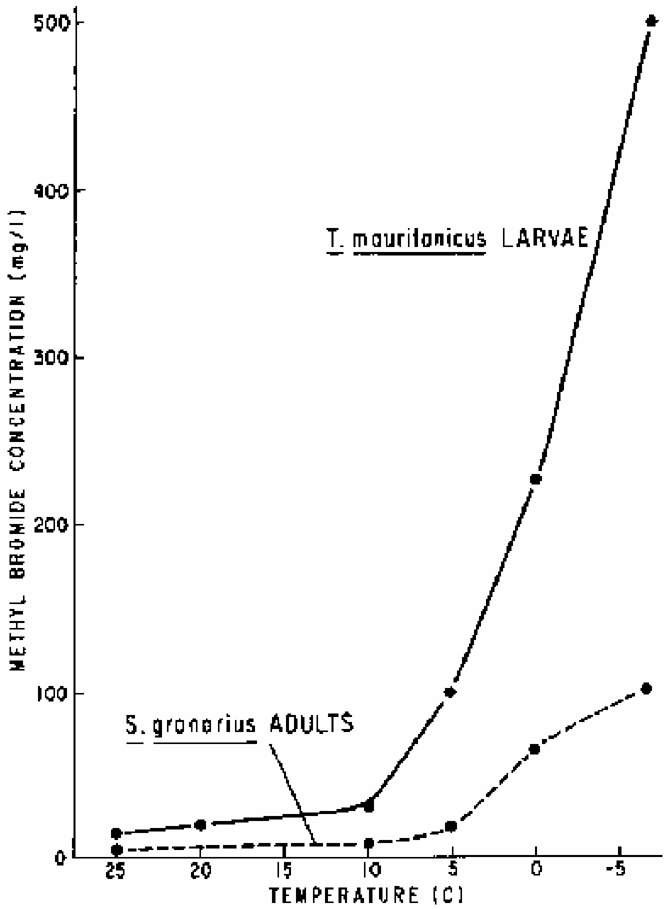
The most important environmental factor influencing the action of fumigants on insects is temperature. In the range of normal fumigating temperatures from 10 to 35°C, the concentration of a fumigant required to kill a given stage of an insect species decreases with the rise in temperature. From the purely biological standpoint, this is mainly due to the increased rate of respiration of the insects in response to the rise in temperature (Sun, 1946). Also, as pointed out previously, physical sorption of the fumigant by the material containing the insects is reduced and proportionately more fumigant is available to attack the insects. Therefore, within the range mentioned, conditions for successful fumigation improve as the temperature rises. These conditions are reflected in the schedules for recommended treatments included in this manual.

Low Temperature Fumigation

At temperatures below 10°C, the situation is more complicated. Below this point, increased sorption of the gas by the body of the insect may counterbalance the effects of decrease in respiration, and also the resistance of insects may be weakened by the effects of exposure to low temperatures. With some fumigants, less gas is required to kill certain species as the temperature is raised or lowered on either side of some point

at which the insects are most tolerant (Moore, 1936; Peters and Ganter 1935; Bond and Buckland, 1976). However, with others, toxicity to the insect's declines as the temperature falls; for example, with methyl bromide there is a moderate decrease in toxicity down to the boiling point and below this temperature effectiveness drops off sharply so that the amount of gas required to kill the insects increases dramatically, as shown in Figure 6.

FIGURE 6. – Mortality (LD'9) of Sitophilus qranarius adults and Tenebroides mauritanicus larvae when exposed to methyl bromide for eight hours at different temperatures.



For the reasons already given in the previous discussion, at lower temperatures sorption of the fumigant by the infested material is increased and more fumigant must be applied to compensate for this. Also, diffusion of a gas is slowed down in relation to reduction in temperature.

Prefumigation and Postfumigation Temperatures

It is important to bear in mind that the results of a fumigation may be influenced not only by the temperature prevailing during the treatment, but also by the temperatures at which the insects are kept before and after treatment.

If the insects have been kept in a cool environment, their metabolic rate will be low. If they are immediately fumigated at a higher temperature, their physiological activity may still be influenced by their previous history, and the uptake of the poison may not be as great as if they had been kept at the temperature of fumigation for a long time previous to treatment (Pradhan and Govindan, 1953-54). These phenomena can be of practical significance, particularly for certain species of insects that may go into a state known as diapause (see Howe (1962) for description of diapause and list of species involved). For insects in this state, tolerance to some fumigants, e.g. methyl bromide and phosphine, may be several times greater than for non-diapausing insects (Bell, 1977 a,b). For other species not in diapause, toxicity is usually found to be closely dependent on the temperature of the fumigation (Bond, 1975; Bond and Buckland, 1976).

A fumigator must have some knowledge of the previous history of the infested material as well as the species to be treated if he or she is to apply the recommended fumigation treatments most effectively. In all treatments, the material should be warmed to the treatment temperature for several hours to bring the insects to corresponding physiological activity before fumigating. If species disposed to the state of diapause are present (e.g. some members of the order Lepidoptera and the families Dermestidae and Ptinidae of the order Coleoptera) the dosage and exposure applied should be increased to a level that will kill the most tolerant insects.

Under experimental conditions, variations in post fumigation temperatures have been observed to influence insect mortalities, but the effects are more complex than those observed in the study of prefumigation temperatures. However, the net contribution of the postfumigation temperature effects would not be of sufficient importance in practice to influence the results of the procedures recommended in this manual. Reference to the papers of Sun (1946) and of Pradhan and Govindan (195354) should be made by those wishing to pursue this aspect of the subject.

Summary of Temperature Effects

From the foregoing discussion it is clear that temperature has far reaching effects on all the factors governing the successful outcome of fumigation. In order to clarify the significance of these effects they may be summarized as follows:

1. For practical purposes, it is increasingly difficult to kill insects with fumigants as the temperature is lowered to 10°C. Below this point, in progression, various species or stages may succumb to low temperature or be weakened by it.

2. Adsorption is the most important physical factor modifying the penetration of fumigants. The amount of gas physically adsorbed increases as the temperature is lowered, and it is necessary to add progressively more fumigant to sustain concentrations free to act on the insects. Furthermore, because of this inverse effect, at low temperatures diffusion of the gas into the material is slower during the treatment, and there is a corresponding decrease in the rate of desorption afterwards.

3. Chemical reaction of the fumigant with some of the fumigated material increases as the temperature is raised. If the residues formed are of significance, it is advisable to conduct the treatment at as low a temperature as possible, with due regard for the handicaps to successful results summarized in paragraphs (1) and (2).

In the light of these three main effects the influence of temperature in different types of fumigation may be considered:

1. With commodities that are easily penetrated and are not highly sorptive, fumigation is practicable at relatively low temperatures with fumigants such as methyl bromide. It will be noted that some of the schedules of recommended treatments at the end of this manual include provision for fumigations at temperatures down to 4°C.

2. Fumigation at temperatures at which the insects are not active may be advantageous in some quarantine treatments. There are two principal reasons for this. Firstly, if seeds or live plants in dormant condition are being fumigated, the risk of injury is reduced by avoiding the possible stimulating effects of higher temperatures on physiological mechanisms. Secondly, if the infesting insects are active fliers, their chances of escape from the material awaiting treatment in a cool environment are greatly reduced.

3. With highly sorptive materials, on the other hand, low temperature fumigation may not be advisable because increased adsorption of the gas by the commodity may interfere with penetration. Also, under some conditions, the material may be hazardous for handling because the adsorbed fumigant is held longer at low temperatures.

EFFECT OF HUMIDITY

From the present knowledge of insect toxicology, it is not possible to make any general statements about the influence of humidity on the susceptibility of insects to fumigants. Variations in response at certain humidity's have been observed not only between different species subjected to different fumigants but also between stages of the same species exposed to a single fumigant. However, variations due to humidity are not as important in practice as those due to temperature.

The treatments recommended in this manual are adequate for the range of moisture content and humidity normally encountered.

EFFECT OF CARBON DIOXIDE

Carbon dioxide, in certain concentrations, may stimulate the respiratory movements and opening of spiracles in insects. A number of authors have shown that addition of carbon dioxide to some of the fumigants may increase or accelerate the toxic effect of the gas (Cotton and Young, 1929; Jones, 1938; Kashi and Bond, 1975; Bond and Buckland, 1978). With each fumigant acting on different insects, there seems to be an

optimum amount of carbon dioxide needed to provide the best insecticidal results. Excessive amounts of carbon dioxide tend to exclude oxygen from insects and thus interfere with the action of the fumigants.

With certain fumigants, such as ethylene oxide and methyl formate, the addition of carbon dioxide may work to advantage both by reducing the fire or explosion hazards and by increasing the susceptibility of the insects. On the other hand, with fumigants that are non-flammable, the advantages of adding carbon dioxide may be offset by the extra cost and work required to handle the additional weight of containers.

The use of carbon dioxide as a "fumigant" introduced artificially into grain storages or other structures is described in Chapter 11.

PROTECTIVE NARCOSIS

Some fumigants can produce paralysing effects on insects that may alter the toxicity of these or other fumigants. In the use of hydrogen cyanide (HCN) against insects, it has been shown that, if certain species are exposed to sublethal concentrations before the full concentration is applied, the resulting fumigation is less effective than one in which the insects are subjected to the full concentration from the very beginning (Lindgren, 1938). A similar protective effect can also occur with the fumigant phosphine if insects are exposed to excessive concentrations during a treatment (Winks, 1974a). Also, insects that have been narcotized by sublethal concentrations of HCN have been found to be protected from lethal treatments with other fumigants, e.g. methyl bromide (Bond, 1961) and phosphine (Bond et al, 1969). This effect has been referred to as "protective stupefaction" or "narcosis".

Although phosphine itself can narcotize insects it does not, however, protect them from the action of methyl bromide as does HCN; in fact, phosphine and methyl bromide can be used together as a "mixture" to enhance the effectiveness of each other (Wohigemuth et al, 1976; Bond, 1978).

From the practical point of view the phenomenon of narcosis is important because it can reduce the effectiveness of certain fumigants. However, steps can be taken to avoid problems of this nature:

1. In fumigations with HCN the maximum concentration attainable from a recommended dosage should be achieved as soon as possible at the beginning of the treatment.

2. HCN should not be applied with other fumigants such as methyl bromide or phosphine, if the maximum toxic effect is to be achieved.

3. Excessive concentrations of phosphine likely to produce a protective narcosis should not be used.

FLUCTUATIONS IN SUSCEPTIBILITY OF INSECTS

It has often been observed that there may be fluctuations in the susceptibility of populations of insects to a given poison. Some of the reasons are known, while others need further clarification. Two important factors are undoubtedly seasonal changes in climate and the effect of nutrition. The susceptibility of insects may be greatly influenced by the quality of the food they consume. It also has been observed with some insects that a certain amount of starvation may make them more, rather than less, resistant to fumigants (Sun, 1946).

In practical work it is well to know that fluctuations in resistance may occur. The alert operator must always be on the lookout for any changed conditions that may necessitate modification of recommended treatments.

COMPARATIVE TOXICITY OF FUMIGANTS

Apart from the influence of the environment, there is a great variation in susceptibility of different species of insects to different fumigants. The successive stages of a given species may also vary greatly in response. Figure 7 illustrates this point. The data were obtained during an extensive study of the usefulness of HCN and methyl bromide for the disinfestation of empty ships (Monro et al, 1952).

Howe and Hole (1966) have shown that these variations in the susceptibility of stages of Sitophilus qranarius (L.), observed under practical conditions, are closely confirmed in laboratory experiments.

A large number of studies have been made under laboratory conditions to determine the relative susceptibility of insects to different fumigants. Table 16 (Chapter 14) shows how fumigants may vary in their toxicity to common species. Bowley and Bell (1981) have reported on the toxicity of twelve fumigants to three species of mites infesting grain.

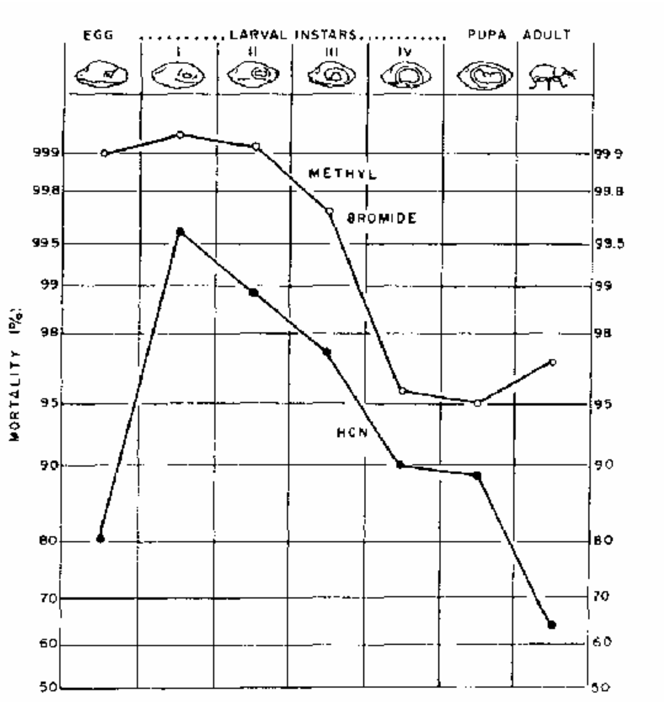
The treatments recommended here are based on laboratory or field trials that have been confirmed, in many instances, by the results of successful application in practice. Note that all recommended treatments refer to specific insects or their stages or, in some cases, to clearly defined groups of insects. There is, therefore, no guarantee of the success of any attempts to apply a treatment outside the limits given in the recommended schedules.

ACQUIRED RESISTANCE OF INSECTS

Many species of insect have the ability to develop resistance to certain insecticides. With fumigants this problem of resistance is a matter of increasing concern; in a global survey of stored grain pests, resistance to both of the major fumigants, phosphine and methyl bromide, was found in a number of insect species (Champ and Dyte, 1976). Collections of 849 strains of insects from 82 countries showed that 20 percent of the

insects had some resistance to phosphine and 5 percent to methyl bromide. The highest level of resistance (10-12 times normal) was found in the lesser grain borer Rhyzopertha dominica (F.). It was concluded from this survey that resistance to fumigants was, as yet, limited in extent and often at marginal levels, but that it was of considerable significance as it posed a real threat to the future use of fumigants as control agents.

FIGURE 7. - The relative susceptibility of different life stages of Sitophilus qranarius to HCN (dosage 0.72 to 0.84 percent by volume) and methyl bromide (0.21 to 0.76 percent by volume) during the fumigation of empty cargo ships. Exposure for 10 to 12 hours, temperature range 3 to 28°C



(Monro et al, 1952)

Research in laboratories has shown that a number of destructive stored product insects can develop appreciable resistance to fumigants. Selection of the granary weevil (Sitophilus qranarius) has produced a strain with more than 12fold resistance to methyl bromide (Bond and Upitis, 1976). A strain of the red flour beetle, Tribolium castaneum (Herbst), developed a 10-fold resistance to phosphine in six generations (Winks, 1974b).

There is recent evidence, from field studies in India and Bangladesh, of the development of resistance to phosphine in the Khapra beetle (Borah and Chalal, 1979) and other stored grain pests (Tyler et al, 1983).

Resistance to fumigants is of concern because of the great value of fumigants for pest control and because of the very limited number of materials available. Even low levels

of resistance in species of insects that are cosmopolitan and easily transported to other parts of the world could be of serious consequence.

In view of the importance of resistance to fumigation, a brief and simplified account of some features of the problem are given below.

HOW RESISTANCE DEVELOPS

When a population of insects is exposed to an insecticide some individuals are killed more easily than others. The insects that are more difficult to kill may survive after the treatment and produce offspring that are also hard to kill. These insects are said to be more tolerant because they can withstand above-average doses of the poison. If a population is repeatedly treated with the same insecticide and each new generation has increasingly higher tolerance, a "resistant" strain is produced. Resistance is a genetic characteristic that is passed on from one generation to the next.

In the laboratory, resistance is produced by treating a population to kill most of the insects, breeding the tolerant survivors to produce a new generation, re-treating and continuing the process until a resistant strain is obtained. This process is known as selection for resistance. A number of strains of insects with resistance to different fumigants have been produced in this way (Monro et al, 1972; Bond, 1973; Winks, 1974b; Bond and Upitis, 1976).

In the field, resistance to fumigants can develop in the same way. In a grain bin, on a cargo ship or any other place where a resident population of insects is treated over and over again with the same fumigant, resistance might develop. Insects that are not killed may produce new generations with increasingly greater tolerance. Generally, resistance does not develop as readily in wild populations as in the laboratory because the selection process .may be irregular and because they may interbreed with non treated susceptible insects. However, the fact that resistance has been discovered in wild populations indicates the possibility that further resistance may develop where fumigants are used regularly.

NATURE OF RESISTANCE

Resistance is an inborn characteristic that allows individual insects to tolerate above average doses of a poison. Resistant insects usually are similar in appearance and have the same habits as susceptible insects. Normally, they can only be distinguished by their ability to tolerate excessive concentrations of the fumigant. Tests have been designed for detecting and measuring resistance to fumigants (FAO, 1975; UK, 1980).

An important feature in resistance is the ability to tolerate the effects of more than one poison. Insects that have resistance to one fumigant can, in some cases, also be resistant to other fumigants. This characteristic, known as "cross-resistance" is demonstrated by the data in Table 5. It can be seen that granary weevils selected with methyl bromide were also resistant to several other fumigants, and the levels of cross-

resistance were all significant in terms of practical control. Such cross-resistance was not found, however, in insects selected with phosphine (Monro et al, 1972; Kem, 1978) or ethylene dibromide (Bond,1973).

TABLE 5. - RESPONSE OF METHYL BROMIDE - RESISTANT GRANARY WEEVIL TO SIX OTHER FUMIGANTS*

FUMIGANT	RESISTANT	NORMAL	TOLERANCE RATIO
Methyl bromide	19.7	3.6	5.5
HCN	16.4	8.2	2.0
Acrylonitrile	4.9	1.05	4.7
Ethylene oxide	20.1	4.1	4.8
Chloropicrin	6.6	3.9	1.7
Phosphine	13.0	2.2	5.9
Ethylene dibromide	8.5	2.85	3.0

*Dosage in mg/l for 5h, at 25°C required for 50 percent mortality (Monro et al,1961).

TESTING FOR RESISTANCE (FAO, 1975)

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 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 Table 6. Susceptible reference strains must always be included in discriminating tests.

When using a discriminating test with fumigants it is always advisable 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 x 1.5 for methyl bromide tests and x 2.5 for phosphine tests. An alternative approach is to use three dosages, one at the discriminating dose, one at the approximate LD(90) level and the other at an equivalent level above the discriminating dose.

In regular monitoring for resistance, it should be detectable even when only a small proportion of resistant individuals is present. A minimum of 100 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 valuable early 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 surviving insects at the end of the test should be regarded as prima facie evidence of resistance and investigated further.

CONFIRMING RESISTANCE

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 (e.g. less than once in 10 tests). It is important to determine whether incomplete response is due to such causes or to genuine resistance. This can be checked as follows:

TABLE 6. – NORMAL SUSCEPTIBILITY DATA OBTAINED FOR METHYL BROMIDE AND PHOSPHINE, WITH DISCRIMINATING DOSAGES.

	LD(50)	LD(99.9)	DISCRIMINATING DOSAGE
METHYL BROMIDE	MG/L		
(Exposure period – 5 hours)			
Sitophilus oryzae (L.)	3.6	4.8	6
S. zeamais Motsch.	3.2	5.4	6
S. qranarius (L.)	5.1	7.5	9
Rhyzopertha dominica (F.)	4.0	7.4	7
Tribolium castaneum (Herbst)	8.4	11.7	12
T. confusum Duv.	8.6	11.2	13
Oryzaephilus surinamensis (L.)	5.8	8.5	9
O. mercator (Fauv.)	5.8	8.5	9
PHOSPHINE (Exposure period – 20 hours)			
Sitophilus oryzae	0.011	0.039	0.04
5. zeamais	0.007	0.013	0.04
5. qranarius	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

1. The test can be repeated 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. If their reaction is actually due to resistance, it will be found that a substantially larger proportion of their progeny will fail to respond to the discriminating dose.

When these tests indicate that a population of insects is resistant, then extensive testing should be carried out to determine the degree of resistance present.

WAYS TO AVOID RESISTANCE

Precautions can be taken to reduce the possibility of insects developing resistance to fumigants.

Perhaps the most effective measure involves alternate control practices that do not require chemicals. Good sanitation procedures, proper storage conditions, insect resistant packaging and all other measures that prevent infestations from developing can do much to reduce the need for fumigants. Treatments such as aeration of the commodity, irradiation, temperature extremes, insect pathogens, etc. as listed in Chapter 1 can also be employed.

Where fumigants have to be used on a regular basis, close guard should be kept against control failures. Complete control of all insects in a treatment is the best insurance against resistance.

Periodic checks for resistance should be made in areas that are fumigated regularly. If signs of resistance begin to appear (as indicated either by control failures or through the test procedure) then every effort should be made to eradicate the population. The measures necessary for eradication will vary in different situations; they may involve a number of procedures using both chemical and non-chemical means.

Rotation of fumigants may be effective in some instances, especially if cross-resistance is not a problem. For example, methyl bromide might be used at intervals in a control programme that relies mainly on phosphine.

One measure that is not advisable in dealing with resistance problems involves increased dosing. Such practices as doubling the dose of fumigant to achieve an economic level of control can magnify the problem unless complete eradication is assured. Any insects surviving increased doses may develop even higher levels of resistance than would occur with the normally recommended treatment.

3. SAFETY PRECAUTIONS AND PROTECTIVE DEVICES

Fumigants are toxic to humans as well as to insects. The claim may occasionally be made by unqualified or irresponsible persons that a certain fumigant is poisonous to insects but harmless to humans. From their very nature as volatile, penetrating and toxic chemicals, all materials used as fumigants can, if not used with proper precautions, poison human beings. Any exposure before, during or after a fumigation treatment can be harmful; hence anyone using fumigants should have some knowledge of their toxic properties and should take every precaution to avoid exposure to them. Nevertheless, if proper care is taken, the work is no more hazardous than any other industrial or domestic technique that uses potentially harmful chemicals.

In this chapter some of the hazardous features of toxic gases are discussed together with general precautions for handling them and protective measures and equipment used to avoid hazards and detect their presence. Special precautions or considerations applicable to individual fumigants or fumigation procedures are given in the pertinent sections of this manual (particularly Chapter 6).

THRESHOLD LIMITS

When handling and applying fumigants it is essential to know for each fumigant the level of concentration above which it is not safe to subject workers and also the maximum periods of exposure, including repeated exposures during normal working hours. Such concentrations are widely known as threshold limits and are usually, and most usefully, expressed in terms of parts per million by volume in air (see Chapter 2 for discussion of methods of expressing concentrations). These threshold limits are published from time to time by responsible authorities or professional organizations in different countries. A comprehensive list for repeated daily exposure is published periodically in the United States by the American Conference of Government Hygienists and may also be found in journals, for example the Archives of Environmental Health, published bimonthly by the American Medical Association.

The purpose and useful interpretation of these limits may best be explained by direct quotation from the most recently published list (ACGIH, 1981):

"Threshold limit values refer to air-borne concentrations of substances and represent conditions under which it is believed that nearly all workers may be repeatedly exposed, day after day, without adverse effect. Because of wide variation in individual susceptibility, however, a small percentage of workers may experience discomfort with some substances at concentrations at or below the threshold limit; a small percentage may be affected more seriously by aggravation of a pre-existing condition or by development of an occupational illness."

Threshold limits are based on the best available information from industrial experience, from experimental human and animal studies and, when possible, from a

combination of the three. The limits should be used as guides in the control of health hazards and should not be regarded as fine lines between safe and dangerous concentrations. The pertinent threshold limits set by this American Conference are given in Table 7 along with a summary of odour thresholds for a number of commonly used fumigants.

Two categories of threshold limit values are given in the Table:

Threshold Limit Value-Time Weighted Average (TLV-TWA), i.e. the time weighted average concentration for a normal eight-hour work-day or 40-hour work-week, to which nearly all workers may be repeatedly exposed, day after day, without adverse effects.

Threshold Limit Value-Short Term Exposure Limit (TLV-STEL) - the maximum concentration to which workers can be exposed for a period up to 15 minutes continuously without suffering from irritation, chronic or irreversible tissue change or narcosis of a sufficient degree to increase accident proneness, impair self-rescue, or materially reduce work efficiency, provided that no more than four excursions per day are permitted, with at least 60 minutes between exposure periods, and provided that the daily TLV-TWA also is not exceeded. The STEL should be considered a maximum allowable concentration, or ceiling, not to be exceeded at any time during the 15minute excursion period. The TWA-STEL should not be used as engineering design criterion or considered as an emergency exposure level.

It is important to realize that if any TLV is exceeded, a potential hazard from that substance is presumed to exist.

Under some conditions, chloropicrin may be used effectively as a pre warning gas in structures, such as ships, where stowaways may be concealed, or in large buildings that are difficult to inspect completely. The pre warming gas is applied separately between 15 to 30 minutes in advance of the main fumigant. A dosage recommended for chloropicrin as a pre warning gas is 6 g/100m^3 (1 oz/15 000 ft^3). It may be applied by soaking the required amount in a cotton or glass wool pad in a glass or metal pan placed in front of a circulating fan to hasten evaporation.

The corrosive and phytotoxic properties of chloropicrin may be important even with the small amounts used for warning purposes.

ACUTE AND CHRONIC HAZARDS

Harmful effects from exposure to a toxic gas may fall into two general categories - acute and chronic.

Acute effects can result from a single exposure to high levels of a fumigant, with symptoms generally appearing within a few minutes or hours. The symptoms will vary with different fumigants and different individuals may be affected differently.

TABLE 7. - ESTIMATES OF ODOUR THRESHOLD AND MAXIMUM EXPOSURES BELIEVED SAFE FOR HUMAN SUBJECTS (VALUES GIVEN IN PPM).

	APPROX ODOUR THRESHOLD	TLV	
		TWA	STEL
Acrylonytrile(2)	20	(2)	-
Carbon disulphide	< 1	10	-
Carbon tetrachloride3	60-70	5	20
Chloroform(3)	200	10	50
Chloropicrin	1-3	0.1	0.3
Dichlorvos	-	0.1	0.3
Ethyl formate	-	100	150
Ethylene dibromide(2)	25	( )	-
Ethylene dichloride	50	10	15
Ethylene oxide(3)	300-1500	(5)	-
Hydrogen cyanide	1-5	10	-
Methyl bromide	none	5	15
Naphthalene	-	10	15
Phosphine	< 14	0.3	1
Sulphuryl fluoride	none	5	10

1 Data on threshold of odour from different sources often differ considerably because evaluation of smell is subjective and somewhat variable. The data on odour threshold should be regarded only as a guide.

2 Listed as human carcinogens by the American Conference of Governmental Industrial Hygienists (ACGIH, 1981). Parentheses indicate proposed values.

3 Listed as "substances suspect of carcinogenic potential for man" (ACGIH, 1981).

4 The odour associated with phosphine appears to be caused by impurities, which can be separated from phosphine under some conditions (Bond and Dumas, 1967; Dumas and Bond, 1974).

Chronic or long-term effects may result from an overdose on a single exposure to a toxic gas or from exposure to low levels over a period of time. The effects may not appear until long after exposure and in some cases they may not be easily associated with the poison. It has been demonstrated that certain of the fumigants can produce

cancer in test animals under experimental conditions. More detailed information on these and other hazardous properties of individual fumigants are given with each fumigant in Chapter 6.

Some fumigants can be absorbed through the skin (including mucous membranes and the eyes) either from the gas or more particularly by direct contact with the substance. When materials are absorbed in this way the threshold limit values given in Table 7, which refer to airborne concentrations of substances, may be invalidated (ACGIH, 1981).

GENERAL PRECAUTIONS

General precautions for the handling and use of all fumigants may be considered under four main headings: preliminary, those taken during application, those taken during the exposure period and post-treatment.

PRELIMINARY PRECAUTIONS

Under this heading may be listed advance precautions of a more general or permanent nature and also preliminary measures applying specifically to each fumigation job.

In any fumigation, large or small, no person should work alone. Because poisonous gases are being used, serious consequences may ensue if a fumigator becomes sick or faint and is unable to finish or control the operation. No matter how small the dosage or the scale of the work, at least one other person should be present in case of emergency.

PRECAUTIONS DURING APPLICATION

In addition to proper respiratory protection, scrupulous care should be taken to ensure that fumigant formulations or liquids do not come into contact with the skin. If clothing or footwear becomes contaminated, it should be removed immediately and affected areas of the skin washed thoroughly with soap and water.

PRECAUTIONS DURING EXPOSURE PERIOD

Every precaution should be taken to avoid exposure to escaping fumigant and to prevent unauthorized entry into treated space. Warning signs that indicate the type of fumigant in use and the date of the treatment should be put in appropriate places. They should be removed after the treatment is completed.

POST-TREATMENT PRECAUTIONS

After adequate aeration of the treated area, gas detection equipment should be used to ascertain that all fumigant has been removed. As the process of desorption can vary greatly with different fumigants, different commodities and different environmental

conditions, precautions should be taken to ensure that harmful levels of gas do not subsequently accumulate where personnel could be exposed.

FIRST AID TRAINING

All members of fumigation crews should be thoroughly trained in basic first aid, with additional emphasis placed on artificial respiration techniques for gas poisoning. Such training is valuable not only for its immediate practical purpose, but also because it serves to emphasize the need for care in all aspects of fumigation.

FIRST AID KIT

All persons engaged in pest control work should carry with them, or have access to, an adequately provisioned first aid kit. Included in this kit should be pertinent information on the nature of poisoning by fumigants or other pesticides used, together with suggestions for remedies. This information would be especially useful to a physician called in to treat an emergency case.

MEDICAL SUPERVISION

It is essential that those regularly engaged in fumigation be under proper medical supervision. The physician should be fully informed of the chemicals used and the manner of their application. Regular medical examinations will check the general health of the operators and reveal the appearance of conditions that may require affected personnel to be removed from this type of work either temporarily or permanently.

INFORMATION FOR PHYSICIANS

It cannot be overemphasized that physicians concerned should be supplied in advance with details of the fumigants used and their toxic effects. The preliminary symptoms of poisoning by toxic gases may be the same as for other common complaints. In addition, occurrences of fumigant poisoning are rare and the average physician is glad to be informed in advance of symptoms and remedies for a condition not ordinarily encountered in common practice.

HOSPITAL FACILITIES

In cities or areas where public hospital facilities are available, it is usually possible to advise the hospital authorities of the possibility of accidental poisoning by fumigants. The staff of the emergency departments may then make arrangements for suitable antidotes to be on hand.

POISON CONTROL CENTRES

Poison control centres are being organized in some countries, and in future they will no doubt become increasingly available in all parts of the world. These centres have been created primarily to deal with the alarming increase in the number of accidents, especially among young children, caused by swallowing the many poisonous substances now available to the public. However, their services may be utilized in emergencies arising out of industrial procedures, such as fumigation work. From these centres physicians may obtain current information on the symptoms and treatment of poisoning. These centres may stock antidotes and even give emergency treatments. In providing for proper medical supervision of their work, fumigators should ascertain, either directly or through their own physician, if there is such a contra situated in their own area and, if so, the nature and extent of the service provided.

ANTIDOTES

If antidotes are recommended as first aid measures for any of the poisons used, they should be purchased and carried in the first aid kit. Even if the antidote may be administered only by a qualified physician, it should be placed in the kit together with any needed accessories, such as sterile hypodermic needles and up-to-date information on the amounts of antidote required, and at what intervals of time. Specific treatments are discussed in detail in Chapter 6. General first aid measures in case of accidents caused by the inhalation or spilling of fumigants are given in Appendix 3.

RESPIRATORS (GAS MASKS)

The respirator is the most important piece of equipment used for the protection of persons working with fumigants. When fumigation is carried out regularly, it is advisable for each of the operators to be supplied with his own respirator so that he himself is responsible for its care and upkeep, for his own personal protection.

The only respirators that should be purchased for fumigation work are those approved for the purpose by a recognized government authority, such as the mines or public health departments, in the country of purchase or manufacture. Such approval usually extends only to a complete assembly. If a certain make of respirator is purchased, the canisters used with it should be obtained from the same manufacturer.

The term respirator is used in many English-speaking countries to describe a device whereby the entire face is covered, or the nose and mouth alone are enclosed, so that the wearer may breathe only filtered air from the surrounding atmosphere; these devices are also called gas masks. Breathing takes place through a filter, which is designed to remove certain contaminants, or through a hose that draws fresh air from outside the space being fumigated. There are also two types of closed circuit respirator available:

- a self-contained unit, using compressed air, carried on the person in one or more small cylinders (bottles);

- a type of self-generating apparatus whereby the oxygen is evolved from a special canister by the action of moisture from the breath.

For most fumigation work the most convenient type of respirator is one that employs a Filter-type canister. This is usually referred to as the industrial type respirator or gas mask; one type is shown in Figure 8. The canister on this type of mask gives adequate protection for a certain length of time from gases that do not exceed a concentration of 2 percent by volume in air (0.5 percent for phosphine); it contains a chemical or physical adsorbent designed to remove contaminant gases from the air being breathed. Canisters are designed to prevent the passage of a particular gas or group of gases. **It is most important to check before each fumigation that the canister on the**

respirator is the right one for use with the specific gas or mixture of gases that will be used for that particular job.

When an operator is applying fumigants and is likely to be working close to the point of emergence of the fumigant from the container, it is good practice to wear the canister on the back, as in Figure 8. This is particularly important when using liquid-type fumigants, as illustrated.

In certain types of fumigation work, such as the spraying of liquid fumigants over large masses of bulk grain, the self-contained types of breathing apparatus, air line masks or the safety blouses (shown in Figure 9), which draw fresh air from outside the building, may be used.

Cartridge-type respirators are small devices with one or two small chemical cartridges attached to the nosepiece. These are usually designed to give protection only against gases up to 0.1 percent by volume. They should not be used in any phase of fumigation work. Also, respirators designed as dust filters, or for use with insecticidal or fungicidal aerosols, afford no protection whatsoever against fumigants. The specific types of canisters recommended for use with particular fumigants or groups of fumigants are listed in Table 8.

When wearing a respirator, a person with punctured eardrums may draw fumigant vapours in through his ears as a result of creating a slight negative pressure during inhalation. Any fumigant drawn this way will be exhaled into the inside of the respirator face piece, and a poisonous concentration may build up inside the respirator. It is usually possible for persons with this defect to obtain complete protection by using cotton earplugs covered with oil.

Men with beards usually cannot fit respirators tightly enough to the face for adequate protection.

Use and Care

Detailed instructions for adjusting, putting on and checking respirators are supplied with each unit purchased. These printed instructions are usually placed inside the lid of the carrying case or in some other convenient place. They should be carefully studied at the time of purchase and read over again before the respirator is used. Supervisors should give new operators detailed instructions on the proper use of the respirators. If a person has not worn a mask before, a regular daily drill should be undertaken to rehearse the proper procedure and movements. This drill should be continued until the new fumigator can demonstrate full familiarity with the correct handling and use of the respirator.

TABLE 8. – TYPES OF CANISTERS USED WITH RESPIRATORS RECOMMENDED FOR RESPIRATORY PROTECTION AGAINST FUMIGANTS.

Compound	Designation of Canister Type	Remarks
Acrylonitrile	OVAG	skin penetrant
Carbon dioxide	AG	oxygen in atmosphere should not be less than 16 percent
Carbon disulphide	OV	skin penetrant
Carbon tetrachloride	OV	skin penetrant
Chloropicrin	OV	skin penetrant
Dichlorvos	OV	skin penetrant
Ethylene dibromide	OV	avoid skin contact
Ethylene dichloride	OV	
Ethylene oxide	OV	
Methyl bromide	OV	skin penetrant
Naphthalene	OV	
Trichloroethylene	OV	
I,I,I – Trichloroethane (Methyl chloroform)	OV	
Hydrogen cyanide	AG	absorbed through skin
Sulphur dioxide	AG	
Hydrogen phosphide	PHOV	not to exceed 200 ppm; above this level supplied air to be used

Notes:
AG – Acid gases
OV – Organic vapours
OVAG – Organic vapours and acid gases
PHOV – Phosphine, organic vapours

THE CANISTER

The canister is that part of the respirator that actually removes the poison from the air breathed in. Therefore its use and limitations must be understood.

Contents and Capacity

Industrial types of canisters which are recommended for fumigation work may contain three kinds of materials:

1. Activated charcoal to adsorb organic vapours, such as methyl bromide, ethylene dichloride and carbon tetrachloride.

2. Chemicals to react with certain gases; for instance, soda lime, which neutralizes acid gases such as HEN and sulphur dioxide.

3. Cotton or other filters to remove dust.

As mentioned above, the manufacturers state on each canister that it is not to be worn in concentrations above 2 percent by volume of the gas in the air. With phosphine, however, the maximum concentration is 200 ppm.

At or near this maximum concentration, which is above fumigant concentrations normally used, the canister will not afford protection for more than 10 minutes. When fumigants such as HCN and chloropicrin, which have a distinct smell, are being used, the operator is warned of the exhaustion of the canister by a slight odour characteristic of the fumigant. Methyl bromide has no odour at comparatively low concentrations and the special precautions needed are included in the discussion of this fumigant.

The possibility of the revivication of canisters containing the activated charcoal used for organic vapours is discussed at the end of this section.

Use and Care

When a canister is new its top and bottom are sealed. Manufacturers stamp an expiry date on the label in order to indicate when the canister must be discarded even if the seals have not been broken.

The supply of canisters should be stored in a cool, dry, well-ventilated place away from contamination by any gases. Before use the following precautions should be observed:

1. When the canister is attached to the respirator after the top seal is removed, the date should be recorded. This is best done by writing the date on a small linen label, which can be tied to the respirator harness near the canister. This label can be used to record the exposure of the canister to the fumigant.

2. If the canister is not exposed to poison gas after the cork is removed, it may be retained in the respirator for one year - but not longer - if stored as above.

3. Before the respirator can be used, it is necessary that the cap or seal over the air inlet valve of the canister be removed. Again, at this time the date should be marked on the label. Once this seal is removed, even if there is no exposure to fumigant, the canister should be replaced after a lapse of six months.

4. After every fumigation operation in which there has been exposure to the gas, the canister should immediately be discarded. **When high fumigant concentrations are encountered in the work, application and aeration should be considered as separate operations, and after each, a fresh canister should be put on the respirator.**

On exposure to lower concentrations, which might be encountered during the aeration or inspection of fumigated structures, the canister should be replaced after two hours, as shown by the label. A wide margin of safety should be allowed in estimating exposure times. Canisters cost little in terms of the health of the individual. If there is any doubt about the exposure life of the canister it should be discarded (see special considerations for methyl bromide in Chapter 6).

5. In addition, canisters should be discarded when any of the following conditions prevail:

– external damage – a severe blow may cause displacement of the contents, permitting contaminated air to pass through to the wearer;

– detection of increased resistance to inhalation – excessive moisture uptake by the canister can impede air flow;

– if lens fogging occurs and fails to clear on inhalation;

– the expiry date is past.

6. Immersion of the canister in water renders it useless. Water may enter the canister through the face piece, so care should be taken that no water enters the hose connexion while the respirator is being cleaned or disinfected.

7. When canisters are discarded, all labels on them should be clearly marked with indelible pencil or black wax pencil "Exhausted" or "Used up". They should be destroyed and immediately sent to the refuse dump under conditions which will prevent them from being picked up and used again.

FINAL CHECKS ON RESPIRATOR

Before any person enters a space where the atmosphere contains a fumigant or undertakes any procedure calling for the use of the respirator, several important points should be checked; these are enumerated below. Also, 8 thorough physical check should be carried out on the proper working of the respirator.

Important Points to Check

1. Is the right canister being used?

2. Is the highest expected fumigant concentration within the absorbing capacity of the canister? (As already stated, industrial canisters are designed for use in gas concentrations not exceeding 2 percent by volume in air. In the tables accompanying the more important fumigants, this value is given in terms of g/m^3 or $oz/l\ 000\ ft^3$).

3. Is the canister in fresh enough condition to give the protection desired? The answer to this should be provided by the record kept on the tag tied to the canister.

4. Even if proper respiratory protection is being given, is there a possibility of gas absorption through the skin? (This consideration was discussed above. Among fumigants, it applies principally to HCN but is also considered later when the different fumigants are discussed).

5. Is there enough oxygen present in the atmosphere to be entered to support normal respiration?

6. Are there other noxious gases in addition to the fumigants? (The ordinary industrial-type canisters used for fumigants will give no protection against carbon monoxide and illuminating gases).

Check for Gas Tightness

After the respirator is put on for actual use with a fumigant, the final check on tightness and proper fit is most important. This is performed as follows:

Place the hand lightly over the air intake at the bottom of the canister and take a deep breath. If the respirator is properly adjusted, a strong draught of air will be felt as it enters the canister.

If the canister is connected to the face piece by a hose, pinch the hose off tightly with the hand. If the face piece is fitting tightly and properly and there are no air leaks, the wearer will not be able to breathe.

If there is no hose, place the hand firmly over the canister intake so that no air can enter. If the respirator is fitted properly the wearer will not be able to breathe.

REGENERATION OF EXHAUSTED CANISTERS

In some countries fresh respirator canisters may be difficult to obtain on account of the problems of supply or foreign exchange. On general principles, as stated above, new canisters should be used for each fumigation job but in an emergency canisters containing activated charcoal only to remove the fumigant from the inspired air may be revived by a regeneration process (Muthu et al, 1964; Maggs and Smith, 1975). If the regeneration process is carefully followed with appropriate testing, it is considered that revived canisters are safe and may be reused for methyl bromide and possibly other fumigants. With the passage of time, however, the activation of charcoal in the

canisters may decline and therefore it is again necessary to stress the importance of adequate testing. For information on regeneration procedures and precautions, the reader should refer to Muthu et al (1964) and Maggs and Smith (1975).

DETECTION OF FUMIGANTS

The importance of having proper equipment for detection of fumigants (down to the threshold limits) cannot be overemphasized. Needless accidents have occurred where personnel were unaware of the presence of a fumigant in the atmosphere; furthermore, relatively low concentrations can be hazardous and the health of workers can be adversely affected.

Several fumigants have little or no odour and even for those having a characteristic odour the sense of smell may not always be reliable AS a means of detection. For safety purposes it is considered essential to have detection equipment that will give reliable and immediate indication of toxic concentrations of fumigants. An outline of the principles of atmospheric monitoring of toxic gases has been given by Thain (1980).

DETECTION DEVICES

A number of instruments or methods are available for the detection of fumigants:

Detector Tubes

Gas detector tubes for determining low levels of several gases are available on the market. These are sealed glass tubes filled with an appropriate indicator chemical to react with a particular gas and give a colour reaction. To make a determination, the seals are broken at each end of the tube and a definite volume of the atmosphere being sampled is drawn through by a hand operated or mechanical pump. The tubes are marked off in scale divisions and the concentration is determined according to the length of discolouration of the indicator for a given volume of atmosphere (see Chapter 6, Figure 18).

Detector tubes are simple, easy to use devices that can provide reasonably reliable, on-the-spot measurement of gas concentrations. Their accuracy may be in the range of 70 to 90 percent of the mean value if sampling is done carefully according to manufacturers' directions. For taking gas samples from difficult locations, extension tubes are available from manufacturers so that the detector tubes can be placed at the desired site.

In addition to these tubes, which give an immediate reaction, long duration tubes for monitoring various toxic gases throughout the normal work day are available. These tubes can be carried anywhere on a worker's clothing in a special holder, while a lightweight pump continuously draws a measured volume of air through the tube. At

the end of the shift, the tube can be evaluated to give a time-weighted average (TWA) of exposure for the working day.

Handbooks that describe in detail the characteristics and capabilities of a wide range of detector tubes are available from some manufacturers (Leichnitz, 1979).

In making use of detector tubes some precautions should be noted:

- Tubes will deteriorate with age - some makes have a shelf life of two years when stored at room temperature; above 30°C deterioration is more rapid.

- Direct sunlight can affect the properties of the tubes.

- At low temperatures, around freezing or below, tubes may not give reliable readings; they should be warmed to room temperature for best performance.

- Tubes may have cross-sensitivity to gases other than those for which they are designed. Information on cross-sensitivity should be obtained from the manufacturer.

Halide Leak Detector

This instrument, which is described more completely under methyl bromide in Chapter 6, is useful for indicating the presence and approximate concentration of methyl bromide, ethylene dibromide or other halogenated compounds in air. It has been used both as a leak detector to locate fumigant escaping from spaces under treatment and as a safety device around fumigation sites. It is also used to check atmospheres for halide fumigant that may desorb from treated commodities.

It should be noted that, while this device is useful for detecting low levels of halogenated fumigants, it may not be safe for detecting potentially harmful concentrations of them. The threshold limit values for a number of fumigants, including methyl bromide, ethylene dibromide and carbon tetrachloride, are below the limits of detection of this instrument.

Infra-Red Analysers

These are instruments that can measure concentrations of gases by the absorbing effect the gases have on a beam of infra-red radiation. Absorption is proportional to path length of the infra-red beam as affected by concentration of the gas. Fumigants have characteristic infra-red absorption spectra that allow both identification and quantitative analysis.

Instruments are available that are ruggedly constructed, but reasonably light and portable so that they can be used in the field for on-the-spot analysis. They are made with scales that read directly in ppm of the fumigant with a reasonable degree of accuracy. The ranges of detection for a number of fumigants are shown in Table 9. Infra-red analysers can be operated with a minimum of instruction by relatively untrained personnel for spot sampling or they can be used for continuous monitoring of atmospheres in the work place.

Although these instruments are relatively expensive, their capabilities for instantaneous detection of low levels of harmful gases may warrant their use in some situations.

Gas Chromatouraphs

Portable gas chromatography are manufactured that can be used for analysis of fumigants in field projects. These instruments also are expensive but they are very effective for both identifying and measuring concentrations of gases at both high and low levels. An instrument (shown in Figure 10) using direct air analysis, which can be easily operated with minimum instruction and can give results in the ppb range (0.001 mg/kg), is available on the market (Barker and Leveson, 1980).

Other Detectors

A number of new devices are being developed for estimating exposure of individuals to toxic gases (McCammon, 1979). These devices have some distinct advantages for personal protection because they are small, lightweight and can be located in the immediate breathing area of the worker. A whole air sampler known as "Critical Orifice Personal Sampler" has been successfully tested for several years and is commercially available. This is an evacuated stainless steel container with a valve allowing air to enter through a micron size critical orifice so that an 8-hour sample can be collected. Once the sample has been collected, the valve is closed and the sample returned to a laboratory for analysis. Several passive monitors that collect samples onto a collection medium are becoming available. A pocket-size gas chromatograph that will provide real-time warning to acute exposures and will accumulate a worker's 8-hour TWA exposure is in the developing stages.

TABLE 9. DATA FOR ANALYSING FUMIGANTS WITH AN INFRA-RED GAS ANALYZER[1]

FUMIGANT	ANALYTICAL WAVELENGTH IN MICRONS	MIN. DETECTABLE CONCENTRATION AT 20.25 METRES[2]	MAX. DETECTABLE CONCENTRATION AT 20.25 METRES[2]	MAX. DETECTABLE CONCENTRATION AT 0.75 METRES[2]
		(PPM)	(PPM) APPROX.	(PPM) APPROX.
Carbon disulphide	4.55	0.5	> 1,450	> 39,200
Carbon tetrachloride	12.6	0.06	> 32	> 870
Acrylonitrile	10.5	0.4	> 330	> 8,900
Chloropicrin	11.5	0.05	> 50	> 1,350
Ethylene dibromide	8.4	0.1	> 300	> 8,100
Ethylene dichloride	8.2	0.3	> 550	> 14,800
Methyl bromide	7.6	0.4	> 945	> 25,530
Sulphuryl fluoride	11.5	0.1	> 57	> 1,543
Phosphine[3]	10.1	1.0	1,000	

1 Foxboro Analytical Company, South Norwalk, CT. 06856, U.S.A.
2 Path length of gas cell
3 Phosphine can be detected at 4.3 microns in concentrations as 0.3 ppm; however, carbon dioxide also absorbs at this same wavelength.

4. FIELD DETERMINATION OF FUMIGANTS

A number of instruments are available on the market for analysis of fumigants under practical operating conditions. Determinations may be conducted at regular intervals both in the free space and in the commodity. Used in conjunction with integrated concentration – time products, as described in Chapter 2, such analyses enable the operator to monitor concentrations throughout a treatment and know when the desired measure of treatment has been attained in all parts of the system. The fumigation may then be terminated at the appropriate time. Apart from the determination of full fumigant concentrations during actual exposure, much of the equipment may also be used to measure the success of the aeration process as indicated by the presence or absence of residual vapours. Some of the equipment may also be used for the purpose of detecting leaks from the structure during treatment.

The methods discussed in this chapter are generally applicable to a variety of fumigants. Specialized procedures are given in Chapter 6 under the headings of the particular fumigants concerned.

THERMAL CONDUCTIVITY ANALYSERS

In recent years a portable instrument known as the thermal conductivity analyser or meter has been used extensively for fumigant determination, principally with methyl bromide. This was first developed for practical use by Phillips and Bulger (1953).

PRINCIPLE OF OPERATION

The basic principle underlying this instrument is that when a constant electric current is passed through a wire, the final equilibrium temperature of the wire is affected by the composition of the gas surrounding it. If the composition of the gas is changed, the equilibrium temperature of the wire will alter. This in turn will alter the resistance of the wire.

In a thermal conductivity apparatus for gas analysis, a Wheatstone bridge circuit is used to measure the imbalance caused by passing gas over the detector filaments. There are usually four or eight filaments in the same number of cells. Half of the cells are used for passing the fumigant/air mixture and the other half, in which only air is present, are used as a control. When an electric current is passed through the filaments, the whole bridge is balanced if the composition of the gases surrounding all the filaments is the same throughout. If the cells surrounding the detecting filaments are filled with a different gas mixture, the bridge becomes unbalanced; the extent of this can be measured by a galvanometer. By calibration with known concentrations of a given gas the galvanometer readings can be transposed into the units of concentration desired, such as 9 per m3.

STANDARD EQUIPMENT

A commercial thermal conductivity analyses has the following components:

1. Four tungsten filaments in as many cells, a pair providing each arm of the bridge. The cells are bored in a brass block. Two cells are used as a control to hold the standard gas, which is air, and the other two are incorporated in the sampling train of the gas-air mixture undergoing analysis.

2. A galvanometer from which readings are made.

3. A potentiometer for current control across the filaments.

4. A separate gas passage for drawing samples through the cells, with inlet and outlet connexions.

5. A source of electric current, which may be provided by batteries contained in the instrument or by connexions to outlets from the local main supply. Direct current of 6 volts is used in the instrument and, if the main supply is used, transformers and rectifiers are needed.

In addition some instruments may contain one or more of the following pieces:

1. An aspirator with a rubber hand bulb for drawing a constant flow of the sample across the cells.

2. An electrically driven pump for the same purpose as in (1).

3. A flowmeter for use when the mechanical pump is used.

4. A guard tube to hold soda-asbestos, or similar material, used to remove water vapour and carbon dioxide from the incoming samples.

In some instruments the reference cells are permanently closed, whilst in others they are open. Sometimes the reference cell is protected by a guard tube, but this is sealed off when sampling begins.

Ideally, it is desirable to take only small samples at a time and an instrument operated by a hand bulb ensures this. When a large structure is undergoing treatment, however, samples have to be drawn from considerable distances and mechanical pumps are necessary.

In practice, the thermal conductivity analyses is unsuitable for use with mixtures of fumigants. It may be possible to calibrate the instrument to indicate concentrations of a mixture in a flask or chamber containing the gaseous mixture only, but in the presence of material being fumigated, the various components of the mixture would be sorbed at different rates and the readings would not provide an accurate indication of the relative proportion of each fumigant present in the free air.

TYPES OF THERMAL CONDUCTIVITY INSTRUMENT

There is a range of instruments available on the market, which vary in accuracy and cost according to the quality of the components incorporated. A bulletin by Heseltine (1961) described in detail the construction and operation of a battery-operated meter, now obtainable commercially, which is of sufficient accuracy to be used in the laboratory and the field. This is shown in operation in Figure 11. A hand bulb is used for aspiration of the sample. (The bulletin contains comprehensive information on many aspects of the use of thermal conductivity meters and anyone employing this technique extensively is advised to study it).

Instruments of the type illustrated in Figure 12 are suitable for large-scale fumigations where accuracy beyond + 0.5 mg/l is not required. They may be operated from the local electricity supply or, for short periods, by a car battery.

A small hand-operated analyses (Figure 13) is available at low cost. This also has a rubber bulb for manual extraction of samples and is powered by an "A" dry battery (6 volts). This is accurate to + 1 mg/l and may be used for periodic checks of gas concentrations in commercial treatments. In field practice this instrument has been found to be reliable as long as the checks discussed below are carried out regularly.

CALIBRATION

It is most important that the thermal conductivity analyser be calibrated frequently against a known concentration of the fumigant or fumigants for which it is being used.

Kenaga (1958) described a simple apparatus, using carbon tetrachloride as the standard gas, for the calibration of the thermal conductivity instrument for various fumigants. Carbon tetrachloride gives the same galvanometer reading as methyl bromide, and since it can initially be measured as a liquid at ordinary temperatures, it is more suitable for calibration.

It is also advisable to check periodically the performance of a thermal conductivity analyses under field operating conditions by taking a series of samples for chemical analysis and comparing the results with instrument readings corresponding in position and time to the origin of the samples. The instrument is then adjusted according to the results of the chemical analysis.

For further details of the design and operation of these analysers and their application in the field for the determination of methyl bromide and other fumigants, the following references may be consulted: Phillips and Bulger (1953); Phillips (1957a); Kenaga (1958); Heseltine et al 1958); Monro et al (1953); Heseltine (1961); Koucherova and Lisitsyn (1962); USDA (1976).

INTERFERENCE REFRACTOMETERS

Instruments designed to utilize differences in the refractive index of gases have been employed successfully for determining fumigant concentrations. In this type of equipment, parallel light from 8 collimator is divided into two beams by two slits and passed through two tubes, into one of which has been introduced the gas mixture under test. The tubes are closed by optically worked glass plates. On emerging from the tubes the two separate beams are brought together by a lens and thus produce in the focal plane of the lens very fine vertical fringes, which can be viewed through an eyepiece. After the zero reading has been set in both tubes in ordinary air, a sample of the atmosphere containing the fumigant under test is drawn into one of the tubes by the squeeze bulb and the difference in the refraction of the gases in the two tubes, as shown by a shift in the fringes, is measured on the scale. By suitable calibration of the readings for a particular fumigant gas, the percentage concentration in the atmosphere under analysis may be easily measured. For greater accuracy in making readings, some operators have found that insertion of a piece of glass capillary tube in the bulb tube will regulate the inflow of gas so that the chosen fringe does not move off the scale. Since the brightness of a fringe can vary according to its position on the scale, this ensures that the same selected fringe is used at all times. An instrument of this type is illustrated in Fig. 14.

Theoretically, an instrument employing this principle gives an absolute reading and is not subject to variable conditions, such as variations in voltage or the failure of component parts to function accurately, which may be encountered with other types of instruments. In practice, such an instrument is simple to operate and readings are reproducible under uniform conditions. However, in common with all apparatus used under field conditions, initial accurate calibration is essential.

Instruments that give different concentration ranges and different degrees of sensitivity are available, the price increasing with the sensitivity of the equipment.

DETECTOR TUBES

Glass detector tubes used for determining the concentrations of a wide range of gases in air are available on the market. These tubes are particularly suitable for use with fumigants which may present a fire hazard under conditions in which a device such as the halide lamp (discussed below) would present a hazard.

The use and accuracy of two makes of these tubes for a number of different gases have been discussed in detail by Dumas and Monro (1966). A more complete description of glass detector tubes has been given in Chapter 3. The employment of the tubes with a number of fumigants is discussed under the heading of each particular gas in Chapter 6.

COLOUR INDICATORS

Colour indicators have been developed commercially for fumigant determination, more particularly with the use of ethylene oxide as a sterilizing agent. These indicators are

tapes placed in or on the material being sterilized, or they may be small sachets containing chemicals which react proportionately to the intensity or duration of exposure. An automatic toxic gas detector that utilizes indicator tapes has been developed for HCN and other toxic gases. This detector is described in more detail in Chapter 6.

Heseltine and Royce (1960) described the application of sachets for both ethylene oxide and methyl bromide fumigations. According to these authors, the sachets used for ethylene oxide may be inspected for the appropriate colour change, either through a window in the treatment chamber or by withdrawal. The methyl bromide sachets give no direct colour reaction and it is necessary to carry out a titration following withdrawal from the fumigation system. With both gases the sachets may be used to determine if a desired concentration x time product has been reached in any part of the system thus ensuring that control of the insects or other organisms has been achieved.

LAMPS

Detector lamps are used, at present, exclusively for halogenated hydrocarbon fumigants. Their best use is for detecting leaks from the system and as a safety check during aeration. They are employed mainly for methyl bromide determination and are discussed under this fumigant in Chapter 6 (see Table 10).

HALIDE METERS

Instruments for measuring low concentrations of halogenated vapours in air, utilizing the principle of photometry, are commercially available.

The intensity of the blue lines of the copper spectrum, produced in an electric arc between two electrodes, is continuously measured with a photo-electric photometer using a blue-sensitive phototube fitted with a blue glass colour filter. Halide vapour coming in contact with the hot tip of the copper electrode reacts to form a copper halide, which vaporizes at the temperature of the electrode and is carried into the arc. The intensity of the blue spectrum is proportional to the concentration of halide vapour present.

These instruments are primarily designed for measuring halogenated hydrocarbons in air from 0 to 500 parts per millions (ppm) with 10 percent accuracy. They are used mainly for safety purposes, but Roth (personal communication, 1967) has found an instrument of this type useful for measuring concentrations of ethylene dibromide up to 7 mg/l in commercial fumigations. For higher concentrations a simple dilution sampling technique is necessary.

Infra-red (IR) analysers

These instruments, described more fully in Chapter 3, can be used for analysing the high concentrations of fumigants needed for insect control as well as the lower levels that may contaminate atmospheres in the work place. They are portable, battery powered, direct reading and have no flame; they can be used safely in dusty atmospheres and are useful for determining whether a space is safe for occupancy. The use of an IR analyser to measure fumigant concentrations in experimental fumigations has been described by Wetzel et al (1977) and Webley et al (1981).

GAS CHROMATOGRAPHS

Portable gas chromatographs are available for gas analysis in field operations (see Figure 10). This instrument is suitable for the high concentrations used for insect control as well as for low concentrations around the threshold limit value for human health (Bond and Dumas, 1982). Although these instruments are expensive, they are accurate and relatively easy to use under field conditions.

5. FUMIGANT RESIDUES

When a pesticide residue remains in food or food products, several factors will determine its importance as a hazard to human health. The average fraction of the total diet likely to contain food with this residue is important, as well as the nature and toxicity of the residue itself.

The following definitions of the terms used in work on pesticide residues are given by the joint FAD/WHO Committee on Pesticide Residues (FAD/WHO 1965a):

Residue: a pesticide chemical, its derivatives and adjuvants in or on a plant or animal. Residues are expressed as parts per million (ppm) based on fresh weight of the sample.

Food factor: the average fraction of the total diet made up by the food or class of foods under discussion. Details of the diet of a country may be obtained from the FAO food balance sheets or other similar data.

Acceptable daily intake: the daily dosage of a chemical which, during an entire lifetime, appears to be without appreciable risk on the basis of all the facts known at the time. "Without appreciable risk" is taken to mean the practical certainty that injury will not result even after a lifetime of exposure. The acceptable daily intake is expressed in milligrams of the chemical, as it appears in the food, per kilogram of body weight (mg/kg/day).

Permissible level: the permissible concentration of a residue in or on a food when first offered for consumption, calculated from the acceptable daily intake, the food factor and the average weight of the consumer. The permissible level is expressed in ppm of the fresh weight of the food.

Tolerance: the permitted concentration of a residue in or on a food, derived by taking into account both the range of residue actually remaining when the food is first offered for consumption (following good agricultural practice) and the permissible level. The tolerance is also expressed in ppm. It is never greater than the permissible level for the food in question and is usually smaller.

NATURE OF FUMIGANT RESIDUES

The kind of residue left after a fumigation may consist of original fumigant, reaction products formed by a combination of fumigant with components of the commodity or end products of a formulation that generates the fumigant.

Unreacted fumigant can remain in some materials for appreciable periods after the treatment. Usually, the amount remaining decreases progressively with time; however, some highly sorptive fumigants such as carbon tetrachloride, ethylene dibromide and

hydrogen cyanide may persist in some materials for weeks or months after airing (Amuh, 1975; Jagielski et al, 1978; Lindgren et al, 1968).

Some fumigants react with components of commodities to form new compounds. Ethylene oxide can combine with the chlorides and bromides in food to form toxic chlorohydrins and bromohydrins (Scudamore and Heuser, 1971). Methyl bromide is decomposed in wheat to form several non-toxic derivatives (Winteringham et al, 1955) and hydrogen cyanide can combine with sugars in dried fruit to form laevulose cyanohydrin (Page and Lubatti, 1948). Other fumigants may also react with materials being fumigated.

In addition to residue from the fumigant, some by-products from formulations such as aluminium phosphide and calcium cyanide can leave residue on food materials. An ash-like residue of aluminium hydroxide, along with a small amount of undecomposed aluminium phosphide, is left after phosphine is generated. Calcium cyanide leaves a residue of calcium hydroxide after hydrogen cyanide is released.

SIGNIFICANCE OF FUMIGANT RESIDUES

The residues remaining in treated materials after a fumigation may be of significance both as an occupational hazard to workers and others exposed to desorbing gas and as a hazard to consumers eating treated foods.

Although desorbing fumigant may not be considered a residue in the usual sense, appreciable amounts can remain for long periods of time and create hazards for personnel in the immediate vicinity. When treated goods are kept in confined spaces, such as airtight bins or a ship's hold, the residual fumigant can be of considerable consequence. There is great concern over the possibility of long-term effects that may develop from exposure to desorbing fumigant.

Some fumigant may remain in food materials and reach the ultimate consumer. Attention has been focused on residues of pesticides in food in recent years because of the harmful effects they may have on human beings. Concern over toxic chemicals in food has been heightened by sensitive detection methods that show traces of residue not previously suspected. The significance of very low levels of some compounds is not known. However, it is believed that the human body can tolerate small amounts without adverse effects. Therefore, residue tolerances are established on the basis of extensive investigation of toxic hazards.

It should be pointed out that numerous surveys for fumigant residues on food have shown only low levels in just a few samples and that cooking normally reduces these to even lower levels. However, concern has been expressed for fumigated foods that are not normally cooked and special recommendations have been given for these situations (FAD/WHO, 1980). In addition, residues that affect food quality through offensive odours or other factors may be of significance. The effect of fumigants on food quality has been reviewed by Plimmer (1977).

Good fumigation practice will normally require that treatments should be conducted in such a way as to keep residues to the lowest possible level.

FACTORS AFFECTING RESIDUE ACCUMULATION

The amount of residue that remains in fumigated materials is determined by the conditions existing during the fumigation and the treatment of the material afterwards. In some cases residue levels may be held to a minimum if the various factors that lead to residue accumulation are taken into account before the treatment is done. A few general statements on residue accumulation can be made. However, it must be emphasized that no one condition is likely to apply equally for all fumigants or for different commodities.

TYPE OF FUMIGANT

Fumigants with high boiling points tend to be sorbed to a greater extent and remain as residues longer than more volatile compounds. For example, acrylonitrile was found to remain in wheat for many days, whereas methyl bromide dissipated in a few hours (Dumas and Bond, 1977). Fumigants that react with plant or animal constituents may also leave appreciable residue. This may be fixed residue such as inorganic bromide, chloride, phosphate or other compound, depending on the fumigant, or it may be a volatile material such as ethylene chlorohydrin from ethylene oxide or dimethyl sulphide from methyl bromide. Solubility in water can also influence residue accumulation. HCN is not used on some moist materials because of the burning effect of the acid formed when it combines with water.

TYPE OF COMMODITY

Some materials will sorb and retain more fumigant than others. Foods with high oil and fat content may retain more residue than cereals. Rhodes et al (1975) indicated that methyl bromide is readily absorbed by lipid materials and they suggest that care should be taken to avoid contamination of high fat content foods such as butter, cheese, margarine, meat etc.

Different fractions of seeds contain different amounts of residue. The shells of walnuts have been found to contain 70 percent of the total residual bromide remaining after fumigation with methyl bromide (Adomako, 1974).

A substantial portion of residual carbon tetrachloride in treated wheat appeared in milled fractions, especially the bran (Jagielski et al, 1978). The gluten fraction of wheat flour contained 80 percent of the total decomposed methyl bromide (Winteringham et al, 1955).

Finely divided materials can often absorb more fumigant and retain more residue than whole seeds. Some materials are not treated with certain fumigants because of the reaction products that remain as residue. Thus, sulphur-containing goods are not

treated with methyl bromide, and materials containing copper or copper salts may react with phosphine, depleting concentrations of the fumigant from the atmosphere and forming undesirable residues.

CONCENTRATION AND EXPOSURE TIME

The amount of residue accumulating during a fumigation can be influenced by the dosage applied and the length of time the material is exposed. The amount of bromide retained by citrus fruit after fumigation with methyl bromide and ethylene chlorobromide WAS found to be greater with higher dosages and longer exposure times (Lindgren and Sinclair, 1951; Lindgren et al, 1968). Similar observations have been made on other commodities treated with methyl bromide, carbon tetrachloride, ethylene dichloride and ethylene dibromide (Whitney, 1963; Rowe et al, 1954).

MOISTURE CONTENT AND HUMIDITY

The retention of sorbed gases and the reaction of fumigants with components of treated goods are influenced by the moisture content of the goods and by the relative humidity of the sir around them. Usually, sorption is higher in materials with higher moisture content. In dried fruit fumigated with HCN, moisture content was found to be the main factor governing retention of cyanide; fruit of 19 percent moisture content retained four times as much free cyanide and had eight times as much laevulose cyanohydrin as fruit of 8 percent moisture content (Page and Lubatti, 1948). Maize at 15 percent moisture content retained twice as much ethylene dibromide as at 9 percent (Sinclair et al, 1964). Humidity of the atmosphere also appears to be an important factor in the dissipation of fumigant. Greater desorption of ethylene dibromide from layers of wheat was found to occur at high rather than low humidity's (Dumas and Bond, 1979).

TEMPERATURE

The rate of desorption of fumigant is usually related to temperature, with less abreacted fumigant residue remaining at high temperatures. However, residue from chemical reaction is likely to be greater at higher temperatures. The inorganic bromide residues in flour increase with increases in temperature, even when the dosage is decreased (Lindgren et al, 1962; Vardell, 1975).

MULTIPLE TREATMENTS

If commodities are refumigated with some fumigants, the level of residue may be expected to increase with each treatment. Cereal grains given repeated treatments with methyl bromide were found to contain increasingly higher levels of inorganic bromide both in the whole grains and in the flour milled from them (Kawamoto et al, 1973; Vardell, 1975; Banks et al, 1976). Similarly, flour fumigated several times with methyl bromide has more residue after each treatment (Brown et al, 1961). On the

other hand, flour refumigated with phosphine contained no more measurable residue than when only treated once (Vardell et al, 1973).

Since there is considerable possibility of re-infestation and subsequent retreatment of goods in international trade, and the history of such treatment may not be known, some precautions may be needed to ensure that the residue levels do not exceed permitted tolerances.

PROCESSING AND COOKING

Milling of fumigated grain will usually remove or reduce residues. All of the residual dust from formulations of aluminium phosphide is entirely removed from grain during the milling process (Liscombe, 1963). Grinding will promote desorption of unreacted fumigant and liberation of volatile reaction products. Chang and Kyle (1979) found that the seed coat offered considerable resistance to desorbing carbon tetrachloride from wheat grains and removal of the seed coat greatly increased the rate of Resorption. However, considerable residue may remain after milling; Heuser (1961) found a large proportion of the residual ethylene dibromide remaining in flour produced from fumigated wheat.

Cooking can further reduce residue levels in most fumigated foods. In the preparation of baked and steamed products from flour treated with ethylene oxide, 20 to 100 percent of the original residue was lost (Scudamore and Heuser, 1971). Residual carbon tetrachloride and ethylene dichloride virtually disappear end most of the free ethylene dibromide dissipates on baking (Jagielski et al, 1978).

However, small amounts of some fumigants can remain after the cooking process. Unchanged ethylene dibromide can be detected in bread, using sensitive analytical methods, and sufficient residues from methyl bromide can remain to cause objectionable odours in bread made from treated flour. For food materials that are intended for consumption without cooking, the withholding period may need to be extended after treatment with fumigants such as ethylene dibromide or carbon tetrachloride, otherwise the food may have to be selected from lots that have not been so treated (FAD/WHO, 1980).

DETECTION AND ANALYSIS OF RESIDUES

For residual fumigants that may desorb from treated material into the atmosphere of the work place, sensitive, easy to use methods of detection are available. These have been outlined in Chapter 3.

The analysis of residues in food and other materials is a highly specialized procedure that is normally done in a laboratory. The techniques used for such determinations are beyond the scope of this manual; however, some information is given under individual fumigants in Chapter 6 and the following publications are given as a guide to sources of more detailed information: FAD/WHO (1980); Alumot and Bielorai (1969); Bielorai

and Alumot (1975); Dumas (1973, 1978, 1980); Dumas and Bond (1975, 1977, 1979); Fairall and Scudamore (1980); Heuser and Scudamore (1968, 1969b, 1970); Jagielski et al (1978); Msjumder et al (1965); Scudamore and Heuser (1971); Stijve (1977).

6. CHEMICALS USED AS FUMIGANTS

In this chapter the more important fumigants are discussed, and condensed information on their pertinent physical and chemical properties is presented. Some fumigants that were used extensively in the past, but have since been replaced by others with more favourable characteristics, are still included to indicate both adverse and beneficial properties. Fumigants having a limited field of use are considered more briefly.

Carbon disulphide and hydrogen cyanide (HCN) were the first chemicals to be used for this type of treatment and HCN remained the primary fumigant for some years. However, with the discovery of methyl bromide and, more recently, phosphine its use has declined significantly. Currently, methyl bromide and phosphine are the most commonly used fumigants for the treatment of stored grain and similar commodities.

METHYL BROMIDE

The insecticidal value of methyl bromide was first reported by Le Goupil (1932) in France. During the 1930s it was widely adopted for plant quarantine purposes because many plants, vegetables and some fruits were found to be tolerant to concentrations effective against the insects concerned. More recently it has been used extensively as an industrial fumigant for stored products, mills, warehouses, ships and railway cars. For this purpose it has now largely replaced hydrogen cyanide. Methyl bromide has also been used as a sterilizing agent, although it has approximately one tenth the activity of ethylene oxide against bacteria and fungi (Bruch, 1961; Richardson and Monro, 1962). Its use for the sterilization of space vehicles in combination with ethylene oxide has been reported by Vashkov and Prishchep (1967). At concentration x time products considerably higher than those needed to kill insects, methyl bromide may also control micro-organisms such as Aspernillus spp. and Penicillium spp. in foodstuffs (Majumder, 1954).

Methyl bromide is not as toxic to most insect species as are some other commonly used fumigants, such as HCN, acrylonitrile and ethylene dibromide. Nevertheless, other properties make methyl bromide an effective and versatile fumigant. The most important of these is its ability to penetrate quickly and deeply into sorptive materials at normal atmospheric pressure. Also, at the end of a treatment, the vapours dissipate rapidly and make possible the safe handling of bulk commodities. Another important property is the fact that many living plants are tolerant to this gas in insecticidal treatments. Methyl bromide is non-flammable and nonexplosive under ordinary circumstances and may be used without special precautions against fire.

Because methyl bromide has a comparatively low boiling point and is not greatly sorbed by many materials, it may be used for low temperature treatments that are not practicable with many other fumigants.

PROPERTIES OF METHYL BROMIDE

Alternative name: monobromomethane

ODOUR	Nil at low concentrations; strong musty or sickly sweet at high concentrations
CHEMICAL FORMULA	CH_3Br
BOILING POINT	3.6°C (38.5°F)
FREEZING POINT	-93°C
MOLECULAR WEIGHT	94.95
SPECIFIC GRAVITY GAS (AIR=1)	3.27 at 0°C
LIQUID (WATER AT 4°C=1)	1.732 at 0°C
LATENT HEAT OF VAPORIZATION	61.52 cal/g
FLAMMABILITY LIMITS IN AIR	Non-flammable (see next page)
SOLUBILITY IN WATER	1.34 g/100 ml at 25°C
PERTINENT CHEMICAL PROPERTIES	Powerful solvent of organic materials, especially natural rubber. When pure, non corrosive to metals. Liquid reacts with aluminium (see text)
METHOD OF EVOLUTION AS FUMIGANT	From steel cylinders under natural or added pressure. Also dispensed from 1 lb cans or 20 ml glass ampoules
COMMERCIAL PURITY	99.4%

Natural vapour pressure at different temperatures

0°C (32°F) 690 mm
10°C (50°F) 1006 mm
Hg 20°C (68°F) 1390 mm Hg
Hg 25°C (77°F) 1610 mm Hg

Weights and volumes of liquid

1 lb (avdp) at 0°C has volume 261.9 ml
1 US gal weighs 14.44 lb (6.550 kg)
1 Imp gal weighs 17.32 lb (7.856 kg)
1 kg has volume 577.36 ml
1 litre weighs 1.732 kg

Dosages and concentrations of gas in air (25°C AND 760 MM PRESSURE)

BY VOLUME		WEIGHT PER VOLUME	
PARTS PER MILLION	PERCENT	[1]G/M³	LB/1000 FT³
20	0.002	0.08	
50	0.005	0.19	
100	0.01	0.39	
200	0.02	0.78	
257	0.026	1.00	
500	0.05	1.94	0.12
1 000	0.10	3.88	0.24
4 121	0.412	16.00	1.00
20 000	2.0	77.65	4.85

[1]Ounce per 1000 cubic feet or milligrams per litre

Treatments of a wide range of commodities may be conducted at temperatures down to 4°c, or even lower in some instances.

At normal fumigation concentrations methyl bromide is odourless. This disadvantage is sometimes overcome by mixing it at the time of packaging with a warning gas such as chloropicrin. The chloropicrin usually constitutes 2 percent of the mixture. Possible pitfalls in the use of chloropicrin as a warning agent are discussed under the heading of this fumigant later in this chapter.

Thompson (1966) has published a comprehensive review of methyl bromide as an insecticidal fumigant. Reference may be made to this for additional information on some aspects of the subject not covered in this manual.

TOXICITY

The effect of methyl bromide on humans and other mammals appears to vary according to the intensity of exposure. At concentrations not immediately fatal, this chemical produces neurological symptoms. High concentrations may bring about death through pulmonary injury and associated circulatory failure. The onset of toxic symptoms is delayed, and the latent period may vary between 0.5 to 48 hours, according to the intensity of the exposure and the personal reaction of the patient (von Oettingen, 1955). Contact of the human skin with the liquid or strong concentrations of the gas may cause severe local blistering (Watrous, 1942).

Against insects, methyl bromide appears to exert its principal toxic effect on the nervous system. As in humans, the onset of poisoning symptoms may be delayed, and with many species of insects definite conclusions as to the success of the treatment should be delayed for at least 24 hours. The comparative toxicity of this fumigant to some stored-product insects is given in Chapter 14, Table 16, and has recently been discussed by Hole (1981).

Richardson and Roth (1965) had some success with this compound against snails in military cargoes (see Schedule T). Methyl bromide is also effective against mites (Acarina). For grain mites, see Barker (1967a,b), and for cheese mites Burkholder (1966). In the treatments in which living plants and flower bulbs are tolerant, the eggs of mites may be resistant and repetition of fumigation may be necessary (see Schedules F and N).

FLAMMABILITY

In laboratory experiments with an intense electric spark, it was found that methyl bromide had a range of flammability from 13.5 to 14.5 percent by volume in air (Jones, 1928). This range has been widely quoted in scientific and trade literature, and the impression has been created that methyl bromide may be flammable or explosive under certain conditions in air. However, in the same series of tests it was found that mixtures of this gas with air in any proportions are non-flammable when ignition is attempted with a flame.

Simmons and Wolfhard (1955) also confirmed that mixtures of methyl bromide and air are non-flammable. Methyl bromide has proved successful as a fire extinguisher (Schleichl, 1961; Fenimore and Jones, 1963; Fish, 1964).

It should be pointed out that, in the absence of oxygen, liquid methyl bromide reacts with aluminium to form methyl aluminium bromide. This compound ignites spontaneously in the presence of oxygen. The explosion of a large tank containing methyl bromide was attributed to the reaction of this compound with the aluminium stem of a measuring instrument beneath the surface of the liquid.

Methyl bromide should never be stored in cylinders containing any appreciable amount of the metal aluminium and aluminium tubing should not be used for application of the fumigant.

EFFECT ON PLANT LIFE

Methyl bromide is one of the few fumigants that may be used safely on a wide range of living plants without producing harmful effects. However, there is a limited number of genera, species or varieties of plants susceptible to injury. Before using this fumigant, therefore, careful attention should be paid to the exceptions listed in the schedules given in this manual. Because chloropicrin is phytotoxic, methyl bromide containing this gas as a warning agent should not be used on nursery stock or other living plants.

Seeds

Methyl bromide has been employed as a seed fumigant because of its ability to penetrate into large consignments of sacks and bags. Under some circumstances, however, treatment with this fumigant has resulted in loss of viability. Also, germination may be delayed or the vitality of young plants impaired. Intensive investigations during recent years have disclosed that injury to germination and retardation of growth of seedlings are directly related to abnormally high temperature, dosage of fumigant, length of exposure and moisture and oil contents of the seed (see Schedule S for a full enumeration of seed treatments and literature references). It may be concluded that, if the seeds are dry enough for safe storage and are not subjected to unnecessarily high temperatures, the dosages and exposure periods given in this manual will be adequate for insect control and will not be likely to cause much damage to the seed. Blackith and Lubatti (1965) laid down a useful general maxim for methyl bromide: "If the seed is dry enough to store, it is dry enough to fumigate." They kept cereal seeds which had been fumigated at 8, 11, 14, and 18 percent moisture content for six years. The seeds were stored at 20°C and at the same moisture content at which they were fumigated. Germination tests were made after 6 months, 3 years and 6 years. For the most part good survival was recorded for both fumigated and nonfumigated seeds at the two lower moisture contents. Rye retained its viability for 3 years when stored dry, but both treated and untreated rye showed almost complete loss of –termination after 6 years.

Powell (1975) tested the tolerance of 40 varieties of vegetable, cereal, fodder and grass seeds with methyl bromide (c x t products of 200 and 400 mg h/l at 10° and 18°C and 10, 13 and 16 percent moisture content) and he concluded that, although the lower values of dosage, temperature and moisture resulted in better germination, most seeds could be safely fumigated at moisture contents below 13 percent and in many cases up to 16 percent. Treatment of vegetable seeds with mixtures of methyl bromide and carbon dioxide and under partial vacuum likewise had no detectable effect on germination (Kononkov et al, 1979).

Repetition of fumigation on a given lot of seed should be avoided, if possible; it has been shown that more than one fumigation may cause reduction in percentages of germination (Strong and Lindgren, 1961). Repeated fumigation can also have adverse affects on the subsequent growth and yield of plants grown from the treated seeds. In tests on white and yellow maize, Joubert and Du Toit (1969) reported that all treatments caused significant reduction in yields from white maize and that, while the apparently hardier yellow maize showed little effect at time of germination, there was a significant reduction in yield after the second and third fumigation.

If repeat fumigation is considered, it is suggested that germination and possibly growth tests be made to determine if injury has occurred during the first treatment. Joubert and Du Toit (1969) advocate extreme caution with the application of fumigants

to seed and they further suggest that a contact insecticide having no adverse effect on the seed should be considered instead of fumigation.

Growing Plants

Methyl bromide may be used to fumigate some growing crops to control pest organisms. The development of light-weight plastic sheets has made it possible to cover sizable areas of land so that the fumigant can be contained for sufficient time to effect a treatment. Large beds of strawberry plants infested with cyclamen mite have been successfully treated in this way (Allen, 1957) and methods for control of European pine shoot moth on ornamental pines have been described (Carolin et al, 1962; Klein and Thompson, 1962; Carolin and Coulter, 1963).

It is estimated that nearly 95 percent of the nursery stock and other plants being moved in commerce are tolerant to dosages of methyl bromide that will kill the insects or other pests involved (Richardson and Balock, 1959). In a few genera of plants, all species may be intolerant while in others only a few species or varieties are known to be affected. Latta and Cowgill (1941) tested 441 species of glasshouse plants with methyl bromide and found that 414 (93.9 percent) were not injured and 27 (6.1 percent) sustained varying degrees of damage; of those, five species were severely burned. In tests on improved citrus stock, Riviello and Rhode (1976) found that exposure to 16 mg/l for 2 hours at 25 – 30°C and 90 percent RH for control of citrus black fly caused little damage to tender growth. A Handbook of Plant Tolerances to Methyl Bromide has been compiled by USDA (1977).

There are several factors that influence the unfavourable response of growing plants to methyl bromide; if they are avoided, even fairly susceptible varieties will be tolerant or, at worst, only lose foliage that will be replaced by new growth. The most important adverse factors are as follows:

1. Low humidity during treatment. Relative humidity in the chamber should be held above 75 percent during fumigation.

2. Dry soil around roots. Less damage is sustained if the soil is moist, mainly because the roots are less susceptible to injury. If there are no insects to be controlled in the soil, it may be completely drenched. Waterlogged soil will not permit the penetration of methyl bromide, and sometimes it is desirable to protect the roots in this way. On the other hand, moist soil allows the rapid penetration of the fumigant.

3. Excessive air currents during fumigation, or during the post treatment aeration period, aggravate injury. It is recommended that circulating and ventilating fans or blowers be operated for the minimum length of time required for distributing the fumigant evenly or for removing toxic concentrations after treatment.

4. Some species of plants may be fumigated only when fully dormant; others are tolerant at any normal stage of growth. The question of dormancy is discussed in the next paragraph and is also covered in Schedules C to F.

Nursery Stock

Plants in active growth are more subject to injury than are dormant plants. As long as plants are fully dormant, there is less danger of damage from methyl bromide, but at the time of breaking dormancy, there may be a period of susceptibility to injury. Coniferous evergreens are particularly liable to sustain severe damage at this critical stage. Great care must be exercised in the choice of the time for nursery stock treatments.

It should be borne in mind that while the failure of subsequent growth of treated plants or any other injury may be attributed to the fumigation treatment, it may also be caused by handling or shipping, as demonstrated by Gammon (1950) and H.H. Richardson (1951) in imported camellia cuttings. Claims that injury to nursery stock is due to the fumigation process should be investigated closely to ascertain whether some other factor or combination of factors may not be responsible.

Recommended treatments for this fumigant on nursery stock are given in Schedules E and F.

Flower Bulbs

Methyl bromide may be used to fumigate narcissus and other bulbs to control insects such as the greater and lesser bulb flies. The treatments effective against these pests do not injure the bulbs (Mackie et al, 1942; Andison and Cram, 1952).

This fumigant is also effective against bulb mites. However, the eggs are resistant to methyl bromide and treatments which are strong enough to kill the eggs are completely destructive to the bulbs. For complete control, the regular treatments may be repeated after 10 to 14 days or when the eggs have hatched. The repetition of the mild treatment causes no injury to the bulbs (Mackie et al, 1942; Monro, 1937-40). Purnell and Hague (1965) reported that fumigations with methyl bromide effective against the stem nematode (Ditylenchus dipsaci Kuhn) are injurious to narcissus bulbs.

The recommended treatments are summarized in Schedule N.

EFFECT ON PLANT PRODUCTS

Fresh Fruit

Methyl bromide has been used widely for quarantine fumigations of fresh fruit. It has been found that some fruits, or certain varieties, are susceptible to injury. The differences in varietal susceptibility are particularly noticeable in apples (Phillips et al,

1938; Phillips and Monro, 1939; Sanford, 1962b; Richardson and Roth, 1966). External damage often takes the form of brown lesions or small round spots on the skin caused by increased or decreased pigmentation in the normal colour of the fruit. Internal injury appears usually as browning of the tissue. With some fruit, ripening and pigmentation are stimulated by low dosages and retarded by high ones. Fruit may vary in susceptibility from one season to another; this is believed to be due to variations in the physiological condition of the fruit. Some workers have been able to detect slight off-flavours or lessening of flavours in fruit subjected to methyl bromide, but it is unlikely that these would be easily detected by the public to the extent that marketing would be affected. The tolerance of deciduous fruit to methyl bromide and other fumigants is discussed fully by Claypool and Vines (1956).

While some fruits are susceptible to injury by methyl bromide, others are tolerant and are treated with this fumigant in quarantine procedures. Methyl bromide is particularly useful when treatments at low temperatures are required. Details of treatments for tolerant fruit are given in Schedule H. It is recommended that fumigation of fruit with methyl bromide should not be carried out on a commercial scale until careful preliminary experiments have indicated that the particular kinds or varieties concerned are tolerant under the full range of conditions likely to be encountered in practice.

At dosages considerably lower than those needed to kill insects, methyl bromide has been successfully used for killing rats and mice in fruit storage units. With the treatments given in Schedule T (Rodents), injury to fruit is not likely to occur.

Vegetables

Both fresh and dry vegetables are generally tolerant to insecticidal treatments with methyl bromide (Roth and Richardson, 1963, 1965).

Schedule I lists tolerant and susceptible fresh vegetables. This fumigant has been used extensively for the treatment of both early and late varieties of potatoes to control the larvae of the tuber moth Phthorimaea operculella. In treatments with concentration x time (c x t) products of 85 mg in/l, which are completely effective against these insects, tubers of all varieties tested at all stages of maturity have proved to be tolerant (Lubatti and Bunday, 1958). Adults and pupae of the Colorado potato beetle can also be controlled without injury to the potatoes (Bond and Svec, 1977).

Sweet potatoes were found by Phillips and Easter (1943) to be sensitive to insecticidal treatments under some conditions. It was noted that newly harvested sweet potatoes were likely to be severely injured, whereas those cured for 15 days or more or kiln dried at 27 to 30°C, were not always injured. Breakdown of cured sweet potatoes after fumigation was associated with postfumigation storage temperatures. Material held at 21 to 27°C was affected less than that moved to ordinary storage at lower temperatures. Proper ventilation after fumigation decreased the amount of the breakdown.

Cereals and Milled Foods

Methyl bromide is widely used for the fumigation of almost every type of cereal and cereal product. Because it penetrates densely packed materials, it is especially useful for the treatment of flours and meals (see Schedule P). Although methyl bromide will react with the protein fraction of wheat (Winteringham et al, 1955), a number of studies have shown that a single treatment at recommended dosages has little or no adverse effect on food value or bread making quality. Even repeated fumigation of wheat stored over a 3year period with a total of 8 treatments caused no significant effect on the vitamin B-6 components (Polansky and Toepfer, 1971) or Tocopherols (Slover and Lehmann, 1972). However, there was a gradual increase in inorganic bromide residue and there were some indications of minor changes in physical qualities of bread made from this wheat. Some members of a taste panel detected a stale aroma in laboratory-type breads and crumbly texture in rolls made from wheats exposed to repeated methyl bromide fumigations (Matthews et al, 1970 a, b).

It has been noted that bread made from flour fumigated with excessive dosages of methyl bromide may have a foreign odour, and if the bread is toasted an unpleasant off-flavour may be produced. Occurrence of this phenomenon is rare and sporadic; Brown et al (1961) reviewed a number of reports of this taint encountered under commercial conditions and carried out a number of tests in the laboratory and they came to the following conclusion:

"It would now appear that some taint is possible even at dosages normally used commercially for insect control. This tainting usually takes the form of abnormal odours when the hot loaves are removed from the oven.

The taste of the bread when cold is quite unaffected at these levels of treatment but a faint odour may still be detected if the bread has been wrapped in polythene or similar material. The avoidance of taint is made more difficult by the likelihood of uneven distribution of fumigant in many types of treatment. However, the risks become very slight if care is taken to limit the level of treatment, if restrictions are placed on repeated fumigation, and if appropriate dilution of fumigated flour by unfumigated flour is arranged where necessary. Over many years very large tonnages of flour have been fumigated with methyl bromide without difficulty and the number of complaints that have come to light is extremely small. These might have been avoided if the precautions suggested had been followed."

As general precautions in the fumigation of flour with methyl bromide great care must be taken not to exceed recommended concentrations or treatment periods; to ensure that even distribution of the fumigant be effected as quickly as possible after the beginning of the treatment and that aeration of the entire stock be conducted quickly and thoroughly immediately on termination of the treatment.

High moisture content of the flour may also be an important factor, as was suggested by the work of Hermitte and Shellenberger (1947) who, however, used excessive doses of methyl bromide greatly above those used in commercial practice.

The only material under this heading barred from fumigation appears to be full fat soybean flour, in which persistent odours and off-flavours may be produced (Dow Chemical Company, 1957).

Nuts and Shelled Nuts

These are treated regularly with methyl bromide, because they are often best suited for bulk treatment (see Schedule P). An interesting and spectacular practice is the treatment of large pyramids of groundnuts awaiting shipment at collecting points in west Africa (Hayward, 1954; Halliday and Prevett, 1963).

Although neither high residues nor taint are produced by normal treatments, excessive dosages or repetitions of treatment should be avoided. Srinath and Ramchandani (1978) reported some off-flavour in walnuts given a second treatment with methyl bromide and more pronounced effects after a third treatment. Shelled nuts with a high oil content, such as cashews, must be treated with particular care. When nuts are stored for prolonged periods in warm weather, fumigation may be repeated. If it is necessary to apply more than two treatments with methyl bromide, a preliminary fumigation of small samples should be made to determine effects on quality.

The problem of treatment repetition may be encountered with importations. Almost invariably, nuts and shelled nuts are fumigated in the country of origin before export, often with methyl bromide. If more than one fumigation is required after importation, there may be danger of taint and a trial treatment should be made.

Dried Fruit

Methyl bromide has been used extensively in recent years for the atmospheric or vacuum fumigation of dried fruit of all kinds. It is well suited for this purpose because it penetrates densely packed materials and diffuses away rapidly after treatment (Page and Luhatti, 1949; Page et al, 1949).

EFFECT ON ANIMAL PRODUCTS

Dairy Products

Methyl bromide is useful for the treatment of dairy products in storage rooms or in convenient atmospheric chambers. It is effective against the cheese skipper, Piophila cased (L.), cheese mites and the grain mite, Acarus siro L., occurring not only on the cheeses themselves but also in infested stores (Dustan, 1937; Robertson, 1952; Searls et al, 1944; Burkholder, 1966). Incidental pests, such as cockroaches, are also easily controlled. Residues in cheese, skim milk powder and butter are generally low. Suggested treatments are given in Schedule P.

Dried Fish and other Animal Products

Calichet (1960) reported that methyl bromide may be user, effectively to control outbreaks of Dermestes beetles in dried fish under African conditions. Similarly, baled animal skins in freight container, have been disinfested with this fumigant (Wainman et al, 1980).

EFFECT UN MISCELLANEOUS MATERIALS

The fumigation of some foodstuffs with methyl bromide may result in the creation of undesirable taints or odours. In some instances they may be attributed to reactions with sulphur or sulphur compounds originally present or added during processing. These odours usually persist intirefinitely and in most cases there is no practical way to remove them. Some of the susceptible materials are not likely to be encountered in strictly agricultural applications of fumigation, but they are listed here so that trouble with them may be avoided.

The following materials should not be expose,) to methyl bromide, or should be exposed only after conducting preliminary tests with small samples (Dow Chemical Company, 1957):

- iodized salt, stabilized with sodium hyposulphite;

– certain baking sodas, salt blocks use d for cattle licks or other foods containing reactive sulphur compounds;

– full fat soya flour;

– sponge rubber

– foam rubber as used in rug padding, pi l lows, cushions and mattresses;

– rubber stamps and similar forms of reclaimed rubber;

– furs, horsehair and pillows (especially feather pillows);

– leather goods, particularly white kid or any other leather goods tanned with a sulphur process;

– wool lens, especially angora; some adverse effects have been noted on woollen socks, sweaters and yarn;;

– viscose rayons, made by a process that uses carbon disulphide;

– cinder blocks or mixtures of mortar; mixed concrete occasionally picks up odours;

– charcoal, which not only becomes contaminated but sorbs great amounts of methyl bromide and thus reduces effective fumigant concert rations;

– paper that has been cured by a sulphide process and silver polishing papers;

– photographic chemicals, not including cameras or films;

– rug padding, vinyl, cellophane;

– any other materials that may contain reactive sulphur compounds.

Methyl bromide decomposes into hydrobromic acid, among other products, in the presence of a flame; this acid is extremely corrosive to metals and destructive to plants.

Where heat is required to raise the temperature for fumigation, steam pipes or low temperature electric strip heaters are recommended. Open flame or high temperature electric heaters should NOT he used (maximum temperature limit is 260°C).

RESIDUES IN FOODSTUFS

Following fumigation of foodstuffs, the greater part of the methyl bromide is desorbed and diffuses away quickly. Under normal circumstances gaseous methyl bromide does not present a residue problem. However, there is usually a small, variable amount of

permanent residue resulting from the chemical reaction between this fumigant and some constituents of the material. The reaction profioct, which is usually easily detectable, is inorganic bromide. In considering this subject it must be borne in mind that many foodstuffs contain natural lie occurring bromides (Heywood , 1966) .

Bromide residues are not likely to he important from the point of view of human health if the foods containing them are consumed in normal amounts. For example, it would require about 135 kg (over 300 lb) of fumigated apples to furnish the average medicinal dose of bromide salt (Phillips et al, l938). However, residues in fumigated nuts much greater than in fruit and vegetables anti problems with flavour or odour can occur. An off-flavour can develop in mesh, bromide-treated nuts upon roasting even though, in some cases, the recommended treatment is followed (Bills et al, 1969). The sequence of events leading to the production of an off-flavour occurs in two steps: first, methyl bromide reacts with methionine in the nuts and second, when the nuts are roasted the product breaks down to release dimethyl sulphide - an odorous sulphur compound. The best way to avoid the problem is through the judicious use of methyl bromide as a fumigant. To ensure that unroasted nuts have not been over-fumigated with methyl bromide, a simple quality control test can be done by roasting a few ounces of the nuts and checking aroma and flavour.

High levels of methyl bromide residue may be of some significance in animal feeds. Cooper et al (1978) and Griffiths et al (1978) reported an adverse effect on egg flavour and a taint in roasted meat from poultry fed on a diet that had been fumigated at high concentrations to eliminate Salmonellae. The off-flavour may result from formation of dimethyl sulphide during the cooking process.

There is also the problem of what happens to the methyl radical, the other part of the methyl bromide molecule, when the residue is formed. As the result of comprehensive experiments on the fumigation of wheat with methyl bromide, it has been concluded that methylation of the protein fraction of the grain is the principal reaction of the methyl radical (Bridges, 1955). Several subsequent studies have shown broad range methylation of protein and free amino acids in cereals fumigated with methyl bromide (FAD/WHO, 1980). The main site of decomposition of methyl bromide in cocoa beans was shown by Asante-Poku et al (1974) to be the alcohol-insoluble proteins, with the greatest amount of breakdown in the shells. Treatment with methyl bromide leads to no appreciable loss of the essential amino acids (Winteringham, 1955) and, although methyl bromide reacts to some extent with vitamins of the B group, such reactions are of no practical importance because there is no significant loss of these vitamins under the conditions of ordinary methyl bromide fumigation (Clegg and Lewis, 1953; Polansky and Toepfer, 1971).

Lynn (1967), in a comprehensive review of the effect of methyl bromide fumigations with respect to methylation of naturally occurring compounds, summarized the subject as follows:

1. Feeding studies with rats and rabbits provide ample evidence that the overall nutritional quality of food is not affected by methyl bromide fumigation. These data also attest to the absence of a health hazard.

2. The essential vitamin-B group is not affected by methyl bromide fumigation.

3. There are indications that the following compounds might be formed by methyl bromide fumigation:

methionine sulphonium methyl bromide
l-methyl histidine
S-methylcysteine
o-methyl compounds

4.Biochemical work has shown that:

- the methionine analogue is found as A naturally occurring component of foodstuffs, is nutritionally equivalent to methionine from the amino acid standpoint end is effective as a transmethylation agent;

- the histidine analogue is commonly encountered in animal and human metabolism and is handled without adverse effect;

- the cysteine apologue is readily metabolized by animals and humans;

- the o-methyl compounds are commonly encountered and accommodated by the animal organism.

A great deal of work has been done on the inorganic bromide residues formed in foodstuffs as the result of fumigation with this compound. Summarized information and literature references are given in the schedules at the end of this manual under the headings of the various types of foodstuffs treated.

<u>Evaluation of Residues</u>

On the basis of toxicological evidence the FAD/WHO joint meeting (FAD/WHO, 1967a) estimated the acceptable daily intake for man of inorganic bromide from all sources as up to 1.0 mg/kg of body weight.

Since residues of bromide ion (inorganic bromide) in foods arising solely from methyl bromide fumigation cannot be distinguished from bromide originating from other sources and a limit of 50 mg/kg would indicate that raw cereals have not been subjected to excessive treatment with methyl bromide, this limit was maintained by the FAD/WHO committee (FAD/WHO, 1980). However, for lettuce and cabbage, where much higher levels of bromide ion have sometimes been encountered, a limit of 100 mg/kg was adopted as an aid to reduction of bromide dietary intake from all sources.

Although no reports of free methyl bromide in goods offered for sale have been published, the dangerous nature of methyl bromide as an alkylating and mutagenic agent indicates that extremely low limits at or about the lower limit of detection are necessary. Therefore guideline levels of 0.0l mg/kg are recommended for commodities at point of retail sale or when offered for consumption (FAD/WHO, 1980).

METHODS OF ANALYSIS

Determination of Vapours

Rough determinations of methyl bromide concentrations in air, for the purpose of detecting serious leaks or for protecting personnel during fumigation and subsequent aeration, may be made with a device commonly referred to as a halide leak detector or halide lamp. These lamps are easily obtainable, usually from refrigeration supply dealers, because they are also used for detecting leaks of the commonly used Freon-type refrigerants. All these lamps work on the same principle, that a flame in contact with a clean piece of copper will burn with a green to blue flame if vapour of an organic halide is present in the surrounding air.

At increasing concentrations of the halide gas, the colour changes from green to greenish-blue or blue. On the basis of this principle it is a fairly simple matter to improvise lamps, given a clean copper wire and a source of flame. Any improvised lamps must, however, he subjected to careful preliminary calibrations.

Various types of detectors are marketed and the difference in construction depends on the fuel they use. Fuels used are, among others, paraffin (kerosene), wood alcohol (methylated spirits, methyl hydrate), acetylene and propane. A lamp using a disposable or a rechargeable canister of propane gas is the most convenient, although it is not as sensitive as those burning paraffin or alcohol. Propane canisters are light, readily available, contain enough gas for about 10 hours' burning and the lamp does not require priming before it is lit.

The use of a propane lamp is illustrated in Figure 15. None of the lamps is to be relied upon for accurate quantitative determinations. They are useful for indicating immediately dangerous concentrations, for checking the effectiveness of aeration after many types of fumigation and for finding leaks during treatment. They should not be used for regular routine checks on the threshold limits for continuous daily exposure to methyl bromide; for this purpose some method of chemical analysis or an accurate recording device should be used.

Reactions of some of the lamps used are shown in Table 10.

Care and operation of lamps. Several considerations are important for the proper and reliable operation of lamps.

1. The copper ring must be kept clean, otherwise a green flame may show in the absence of methyl bromide.

2. The flame must burn through the ring, not around it; if the ring is clean, and the air is free of fumigant or dust, the flame should be invisible above the ring.

3. After some time the copper ring deteriorates and must be replaced by a new one.

4. These lamps are not specific for methyl bromide; they react to any organic halogen gas, such as the Freon refrigerants, whose presence in the air may result in erroneous lamp readings. It is advisable to test atmospheres before the fumigant is applied to ensure that no interfering substance is present.

5. Obviously, the lamps cannot be used in the presence of flammable or explosive gases, such as gasoline vapours, or with some organic halide gases, such as methyl chloride and ethylene dichloride, which are also flammable and may be used as fumigants.

6. Lamps should not be used in dust-laden atmospheres. If gas analysis is required from such areas, a sample of the atmosphere may be obtained by opening a polythene bag at the point to be checked and removing the sample to a safe location. Alternatively, a sample may be drawn from the treated area through plastic or copper tubing to a suitable outside area.

7. Colour blind persons cannot detect colour changes in a halide detector flame.

8. If used at night the gas detector flame will have a bluish cast; hence, appropriate allowance for variations in different light conditions should be made.

TABLE 10 – APPROXIMATE COLOUR REACTIONS OF HALIDE LEAK DETECTOR LAMPS

CONCENTRATIONS OF METHYL BROMIDE IN AIR	REACTION OF FLAME
Parts per million	
0	No reaction
10	Very faint green tinge at edge of flame
20	Light green edge to flame
30	Light green flame
100	Moderate green
200	Intense green, blue et edge
500	Blue green
1 000	Intense blue

Note: Owing to variations in response of individual lamps, readings below 30 ppm are unreliable.

Gas detector tubes. Where a more precise measurement of the concentration in the region of the threshold limit value is required, a simple method is the use of a gas detector tube as described in Chapter 3. Tubes for methyl bromide are available from several manufacturers in ranges from 2 – 200 ppm and they should be used strictly in accordance with instructions. A fresh tube is required for each determination.

Infra-red analyser. This detector will measure concentrations of methyl bromide well below threshold limit values. It is portable, battery powered, direct reading and has no flame to cause hazards in dust laden atmospheres. This instrument can be used to determine if buildings or other spaces are safe for occupancy.

Gas chromatography. The portable gas chromatograph described in Chapter 3 will readily analyse methyl bromide at working levels used in fumigation and at low levels down to 0.01 ppm and below.

Thermal conductivity analyser. The thermal conductivity analyser is fully discussed and described in Chapter 4. Instruments of this type are particularly suitable for use with methyl bromide and are, in practice, used mainly with this fumigant. However, they are not sensitive enough to determine the health hazards presented by low concentrations of methyl bromide and are not authorized for this purpose in fumigation codes of safety.

Chemical analysis. A convenient method of chemical analysis for field use is the Volhard titration after the gas has been absorbed in monoethanolamine. Chemically pure monoethanolamine, in the amount of 2 ml for each 0.45 kg (1 lb) of methyl

bromide per 28 m' (1 000 ft^3) in the fumigation space, is placed in a glass bottle fitted with a stopcock. The glass bottle must be able to withstand evacuation; round 1-litre (quart) bottles have been used successfully. The stopcock is connected to copper or polyethylene tubing that leads from the desired sampling points in the fumigation system. Before a sample is taken, the bottle is evacuated to a pressure of 1 to 2 cm. The flask should stand for at least 2 hours before the titration is started. The bromide is estimated after it has been precipitated by excess standard silver nitrate solution; the excess silver is titrated by standard potassium thiocyanate, ferric alum being used as an indicator. Full details of this method are given by Brown (1959) and may also be found in standard works on the analysis of insecticides (Jacobs, 1949; Gunther and Blinn, 1955).

Other field methods. The interference refractometer described in Chapter 4 is suitable for determining concentrations of methyl bromide during fumigation.

The sachets described by Heseltine and Royce (1960) and discussed in Chapter 4 are also useful for estimating elapsed concentration x time products during an actual treatment.

Laboratory analysis. The Volhard titration method given above is suitable for laboratory determination of vapours. Dumas and Latimer (1962) described a method for analysing the vapours by a technique of coulometric titration whereby amounts as small as 17 µg of methyl bromide in a sample may be determined accurately. Berck (1965a) listed methyl bromide among the fumigants which may be determined by gas chromatography.

Determination of residues

Mapes and Shrader (1957a) gave a chemical method for determining total and inorganic bromide residues in fumigated foodstuffs. The basis of this method is that the bromides are hydrolysed with ethanolamine and the alcohol is removed by evaporation. The residue is ashed with sodium hydroxide and sodium peroxide. The bromide is leached from the ash and determined by the KolthoffYutzy-van der Meulen method. Total bromide ion may also be determined by xray fluorescence (Cetzendaner et al, 1968) or by neutron activation analysis (Lindgren et al, 1962).

Selective determination of bromide ion may be carried out with a selective ion electrode (Banks et al, 1976) or by using gas chromatography (Heuser and Scudamore, 1970; Panel on Fumigant Residues in Grain, 1974; Stijve, 1977).

Determination of free methyl bromide in commodities can be carried out by various methods using gas chromatography (Heuser and Scudamore, 1968, 1969b; Greve and Hogendoorn, 1979; Fairall and Scudamore, 1980; Dumas, 1982).

APPLICATION

Containers

Methyl bromide is supplied by manufacturers in the following types of containers:

- Steel cylinders with capacities from 5 to 1 800 lb (2.25 to 816 kg). For ordinary field purposes, the 50- or 100-lb (23- or 45-kg) sizes are the most convenient. The cylinders have siphons and at normal temperatures the natural vapour pressure of the fumigant is sufficient to discharge it from the cylinder. Some manufacturers inject an inert gas, such as nitrogen, under pressure into the space above the liquid before the cylinder is shipped; this helps to force the fumigant through lines of piping. Other makers supply additional valves on the heads of the cylinders so that more pressure from compressed nitrogen or air may be applied at the time of discharge.

To apply the desired quantity of fumigant from a cylinder, a set of scales is used to determine the amount being discharged (Figure 16). Spray nozzles, as described by the U.K. Ministry of Agriculture, Fisheries and Food (UK, 1974) or a sprinkler as outlined by Calderon and Carmi (1973) have been found useful for dispersing the fumigant in large spaces.

- Cans containing 1 or l.5 lb (0.45 or 0.68 kg) of the fumigant. Some manufacturers make 0.5 lb cans available on request. A special device (Figure 17) for discharging the fumigant from them under natural pressure is obtainable from the supplier and copper or plastic tubing may be attached to carry the methyl bromide to the space being fumigated, as required. This method of application is useful for small-scale operations because the cans are easy to handle and the dosages are easy to compute in terms of the number of cans required. An opened can must be completely emptied as it cannot be resealed.

If the fumigant is discharged as a gas from the can, considerable cooling of the liquid takes place, especially in cool weather, and the temperature may fall below the boiling point of methyl bromide (3.6°C). If the can is immersed in a pail of hot water (not above 77°C), the fumigant is discharged more evenly and rapidly.

- Glass ampoules, usually containing 20 ml of methyl bromide, are supplied by some manufacturers. These are useful for small chambers, such as the drum fumigator described in Chapter 8 and illustrated in Figure 27. A plunger or similar device is needed for breaking these ampoules so that the fumigant can disperse in the chamber.

Discharging methyl bromide

As already suggested, freezing of the tubes and piping carrying the fumigant sometimes occurs due to the loss of heat from evaporation. This is more likely to occur when the fumigant is carried some distance from the container. In many applications, therefore, the fumigant is led through a heat exchanger after it leaves the container. For small dosages, a suitable exchanger is a hot water bath or pail in which is coiled 15 m (50 ft) of copper tubing. (This method is unsuitable with cans because back

pressure develops against the fumigant still in the can; the entire can must be immersed, as described previously.)

For large-scale operations, a greater transfer of heat is required. Several devices have been described in detail by Hammer and Amstutz (1955). The essential feature of these heaters is a vaporizing chamber of sufficient capacity to convert the liquid methyl bromide into yes as it passes through. At temperatures below 15°C or when large quantities of methyl bromide are used a vaporizer, a 15 m coil of copper tubing, 10 - 15 mm in diameter, immersed in a container of water heated to 65 C may be required. The fumigant should be passed through the tubing at a rate of 1 - 2 kg per minute and liberated as a vapour into the air stream of a fan or blower (USDA, 1976). Any convenient and safe source of heat may be utilized for these heaters. Bottled propane and live steam have proved successful. Heat from a flame or electrical heater should not be applied directly to the vaporizing chamber, which should always be surrounded by hot water. The water bath, if closed, should have a water gauge and a safety valve.

Evaporating pans When methyl bromide is discharged into a fumigation chamber, a good practice is to let the liquid flow into a shallow evaporating pan of sufficient capacity to hold the entire dosage at a depth not greater than 12 mm (0.5 in). In this way, more even distribution of the fumigant is obtained, especially if a current of air from a fan or blower is directed across the pan; also, the danger of liquid spilling directly on the commodity is eliminated. If fumigation is being effected at temperatures below 15°C, the pan may be warmed in some way, preferably with heating coils, infra-red heaters or ordinary light bulbs.

Precautions in discharge Although methyl bromide is non-flammable, in the presence of a flame it breaks down quickly to hydrobromic acid. This is highly corrosive to metals and destructive to plants and plant materials. Therefore, during methyl bromide fumigation the space should not be warmed by heaters with exposed glowing wires. Also, all pilot or other flames should be extinguished before fumigation begins. The corrosive effect is greatly increased under warm, humid conditions.

Measurement of Dosage

Fractional measuring devices are used when the dosage of methyl bromide cannot be computed in terms of whole cylinders or cans. Sometimes the approximate dosages discharged from cylinders can be determined by weighing the cylinders on portable scales. Graduated glass measuring tubes (such as the one shown on the top of the drum fumigator in Chapter 8, Figure 27) are accurate to the nearest millimetre and are used for measuring amounts up to 280 ml (the volume of l lb of methyl bromide is 260 ml at 0°C). For very small quantities a method for tapping a 454 kg (l lb) can and extracting measured amounts in a gas syringe has been described (Buckland and Bond, 1973) (see also Chapter 14).

PRECAUTIONS

Concentrations Toxic to Humans

Persons should not be exposed continuously to concentrations of this gas in excess of 5 ppm. This is the threshold limit for an 8-hour daily exposure suggested by the American Conference of Government Industrial Hygienists (ACGIH, 1981).

From experiments with animals and records of accidents to human beings, it appears that daily exposure to concentrations of 20 to 100 ppm of methyl bromide can quickly bring about severe neurological symptoms, described below under "First aid". Exposure for only a few hours to concentrations of 100 to 200 ppm may cause severe illness or death. It is not advisable, therefore, for persons to remain in any atmosphere which gives a positive reaction for methyl bromide in the flame of the detector unless properly protected by a respirator.

Blood Tests

It has been suggested by Torkelson et al (1966) that persons continuously engaged in fumigation with methyl bromide should have checks at least once a month to determine their blood bromide levels. Such tests would give reassurance of safe practices if no undue rise in blood bromide levels were observed. On the other hand, if a person becomes ill an immediate test would indicate whether the sickness could be attributed to the fumigant. Furthermore, any significant increase from the normal level found during the routine tests would serve as a warning of undue exposure to the fumigant and the necessary precautionary steps could be taken.

If there has been no other source of bromide, such as medications or drinking water, a level above 15 mg percent indicates dangerous exposure. A level below 5 mg percent indicates mild or no exposure and symptoms would be unlikely. Such a regime of testing should only be undertaken after consultation with a qualified industrial toxicologist. Determination of bromides in blood and spinal fluid may be made by methods of Paul et al (1952) or Hunter (1953).

Respiratory Protection

During any phase of a fumigation operation where there is likelihood of exposures to methyl bromide above 5 ppm, appropriate respiratory protection must be taken. It is important to remember that methyl bromide may be odourless and, if a canister-type gas mask is used, the length of time the correct canister (organic vapours) can afford protection must be estimated. This time should be calculated from the concentration corresponding to the actual dosage applied and a high rate of breathing. Table 11 is drawn up on this basis. The suggested lengths of time given in this table apply only to methyl bromide or a mixture of 98 percent methyl bromide and 2 percent chlaropicrin.

It is recommended by manufacturers of safety equipment that with methyl bromide the respirator canisters be discarded after only one exposure to this fumigant. This precaution is due to the fact that methyl bromide may continue to diffuse through the

activated charcoal filling of the canister even when inspired air is not being drawn through it. The only possible exception is that, if the canister is used in concentrations of less than 50 ppm in air and the concentration never exceeds this, it would be permissible to use it during a continuous 8-hour period. Such provision would permit the use of the canister during an aeration procedure when only low concentrations, below 50 ppm, would be encountered (Merkle, 1967, personal communication). Regardless of the number of exposures, the canister should be discarded at the end of 8 hours.

Because 80 g/m^3 (5 lb/1000 ft^3) are equivalent to 2 percent by volume in air, the respirator cannot be guaranteed3to give protection from a dosage of more than 64 g/m (4 lb/1000 ft). When interpreting the figures given in Table 11 the dosages and times should be overestimated in order to allow the greatest possible margin of safety.

TABLE 11 - SUGGESTED MAXIMUM TIME A RESPIRATOR CANISTER SHOULD BE USED IN METHYL BROMIDE FUMLGATION(CANISTER OF THE TYPE USED I-OR ORGANIC VAPOURS)*

CONCENTRATION OF METHYL BROMIDE G/M³ (OZ/L 000 FT 3)	MAXIMUM TIME** MINUTES
16 or less	60
16 - 32	30
32 - 48	22
48 - 64	15

* This applies to a standard size canister for only one exposure to the fumigant vapours (see text)
** Based on recommendations of Dow Chemical Company (undated).

As pointed out previously, -in sound fumigation practice there should be little exposure to fumigant concentrations. Self-contained respirators, airline respirators, safety blouses and head-to-toe protective suits may also be used to give protection. Methyl bromide is listed as a compound that may be absorbed through the skin as well as by the respiratory system. In a properly planned fumigation of a building, the operator releasing the gas should keep moving away from the initial high concentration. During aeration, the operators usually wait for some time after as many doors and windows as possible have been opened and the ventilators or blowers started. After entering the structure, the operator is thus exposed to rapidly falling concentrations.

Absorption of Vapours through Skin

Medical literature contains references suggesting that methyl bromide poisoning may follow absorption through the skin. It is, however, probable that this may not occur in exposure to concentrations and times given in the preceding paragraph, for which protection is given by the respirator (Butler et al, 1945).

Contact of Liquid with the Skin

Prolonged contact of liquid methyl bromide with the skin produces severe blisters similar to those caused by burns or extreme chilling. Great care should be taken to avoid spilling liquid methyl bromide on clothes or footwear. Leather or rubber boots, shoes and gloves are likely to retain the liquid and hold it in contact with the skin. Since there is no particular sensation produced by such contact, methyl bromide may be maintained in contact with the skin for extended periods without an awareness that this has occurred.

As soon as possible after methyl bromide is spilled on clothing or footwear, it should be removed and thoroughly aired. If methyl bromide has remained in contact with the skin so that blisters form, the blisters should be left intact and the area covered with a sterile petrolatum dressing. When working with methyl bromide, gloves, bandages or occlusive dressings should not be worn. If liquid is spilled on the hands lower arms or other exposed areas of skin, it will evaporate quickly. However, the parts touched should be washed with soap and water immediately.

FIRST AID

There is no known antidote for methyl bromide poisoning. Also, because the onset of symptoms is usually delayed, there are no specific procedures to bring about immediate recovery. However, there are certain well-defined symptoms which, except in cases of exposure to high and rapidly fatal concentrations, may serve as preliminary warnings of initial poisoning. If, on experiencing these symptoms, the fumigator immediately abstains from further contact with methyl bromide and places himself under medical supervision, there is every prospect of complete recovery.

If any of the symptoms listed below are experienced during or after exposure to methyl bromide, the person affected should leave the vicinity and report immediately to a physician.

Important. **These symptoms may be delayed for periods up to 45 hours** (von Oettingen, 1955).

Possible symptoms of methyl bromide poisoning are:

nausea and vomiting
loss of appetite
dizziness
abdominal pain
double or blurred vision
impaired, slurred speech
unusual fatigue
mental confusion
headache
convulsions

If the affected individual is seriously poisoned, it is advisable for all other members of the crew to place themselves under medical observation immediately.

The following measures are recommended for administration under medical supervision (Dow Chemical Company, 1964).

Notes to the Physician

Nausea and vomiting can be a most distressing part of the symptom complex from methyl bromide exposure and may require one of the anti-emetic drugs. Support of the respiratory system will dictate a semi-recumbent position, maintenance of a free airway and possible tracheostomy. Oxygen should be used at the first sign of respiratory embarrassment and if pulmonary oedema develops. Intermittent positive pressure breathing may be helpful. If respiration fails, artificial respiration by an appropriate means may be necessary. Central nervous system effects are extremely difficult to control. tlyperexcitability and convulsions may require either a barbiturate, such as pentobarbital (Nembutal), or diazepam (Valium). Respiratory depression must be guarded against. Diazepam may be given in 5 to 10 mg doses by slow intravenous injection.

Severe seizures may be controlled by slowly giving pentobarbital intravenously in doses up to 5 my/kg of body weight. Caution: Respiratory depression must be watched for in the use of these drugs.

Circulatory failure may be combated by intravenous solutions and levarterenol bitartrate .

Individuals surviving the first two or three days will probably recover. Central nervous system symptoms may persist for weeks or months, occasionally even as much as a year. However, eventual recovery is the rule.

Although the treatment of methyl bromide intoxication is usually symptomatic, there is some evidence that early haemodialysis may be helpful. Dimercaprol (BAL) is sometimes recommended as an antidote, but the rationale for this approach is unclear. There are unconfirmed reports from Japan suggesting that pantothenic acid in large doses may be helpful in treating residual neurological symptoms.

Burns resulting from skin contact with the liquid material should be treated like thermal burns following decontamination.

Liver and kidney damage is quite unlikely in the absence of severe respiratory or central nervous system effects.

A blood bromide level should be obtained immediately on any individuals suspected of being exposed to methyl bromide.

PHOSPHINE

Phosphine or hydrogen phosphide (PH_3) is a low molecular weight, low boiling point compound that diffuses rapidly and penetrates deeply into materials, such as large bulks of grain or tightly packed materials. The gas is produced from formulations of metallic phosphides (usually aluminium or magnesium phosphide) that contain additional materials for regulating release of the gas.

$AlP + 3H_2O$ □ PH_3^ + $Al(OH)_3$

$Mg_3P_2 + 6H_2O$ □ $2PH_3$^ + $3Mg(OH)_2$

Aluminium phosphide is formulated 8S tablets, pellets or small sachets of powder with additional materials such as ammonium carbamate, ammonium bicarbonate, urea and paraffin to regulate release of fumigant and suppress flammability. The magnesium phosphide is similarly manufactured in tablets or pellets. It is also prepared in flat plates; here the formulation is embedded in a plastic matrix that regulates access of moisture and hence controls release of the gas. After the phosphine has evolved from a formulation, the residue that remains consists mainly of aluminium or magnesium hydroxide. Small amounts of undecomposed aluminium phosphide may also remain in the grey white dust from tablets, pellets or sachets.

PROPERTIES OF PHOSPHINE

Alternative name: hydrogen phosphide

ODOUR	Carbide or garlic-like odour may be due to impurities (see text)
CHEMICAL FORMULA	PH_3
BOILING POINT	-87.4°C
FREEZING POINT	-133.5°C
MOLECULAR WEIGHT	34.04
SPECIFIC GRAVITY GAS (AIR = 1)	1.214°
LIQUID (WATER AT 4°C = 1)	0.746(-90)
LATENT HEAT OF VAPORIZATION	102.6 cal/g
LOWEST EXPLOSION POINT	1.79% by volume in air
SOLUBILITY IN WATER	26 cc/100 ml at 17°C (very slightly soluble)
METHOD OF EVOLUTION AS FUMIGANT	From preparations of aluminium and magnesium phosphide
PERTINENT CHEMICAL PROPERTIES	Reacts with copper and precious metals.

Natural vapour pressure at different temperatures

0°C (32°F) 21.6 atmos
20°C (68°F) 34.2 atmos
40°C (104°F) 51.9 atmos

Dosages and concentrations of gas in air (25°C AND 760 MM PRESSURE)

BY VOLUME		WEIGHT PER VOLUME	
PARTS PER MILLION	PERCENT	[1]G/M³	LB/L 000FT³
[2]0.3	0.00003	0.0004	
20	0.002	0.03	
50	0.005	0.07	
100	0.01	0.14	
200	0.02	0.28	
500	0.05	0.70	
718	0.072	1.00	0.04
1 000	0.10	1.39	0.087
11 493	1.15	16.00	1.00
20 000	2.0	27.84	1.74

[1]Ounces per 1000 cubic feet or milligrams per litre
[2]Threshold limit, ACGIH, 1981.

A strong odour, resembling carbide or garlic, is normally associated with the evolution of phosphine from various formulations. It can be detected by smell even at very low concentrations. This odour seems to be due to the presence of other compounds produced along with phosphine and they may be preferentially absorbed during fumigation treatments. Under some conditions the odour may disappear, even when insecticidally effective concentrations are still present in the free space of a fumigation system (Bond and Dumas, 1967; Dumas and Bond, 1974). While any odour associated with the evolution of phosphine may indicate the presence of phosphine, it should not be relied on for warning purposes.

TOXICITY

Phosphine is very toxic to all forms of animal life, hence exposure of human beings even to small amounts should be avoided. Poisoning can result from ingestion or inhalation; however, the gas is not absorbed through the skin. A concentration of 2.8 mg/l (ca 2 000 ppm in air) is lethal to humans in a very short time (Flury and Zernik, 1931). The threshold limit value is usually set at 0.3 ppm for a 40-hour work week. Symptoms of poisoning for humans are described below under "First Aid".

Phosphine ranks as one of the most toxic fumigants of stored product insects (see Chapter 14, Table 16). It is a slow acting poison that is effective at very low concentrations if the exposure time is long enough. Usually, exposure times of four or more days are required to control insects, depending on temperature. The toxicity of

phosphine to insects declines as the temperature falls to 5°C, so that longer exposure times are required for it to exert its effect. It is not recommended for use below 5°C. The exposure time cannot be shortened by increasing the dosage; in fact, high concentrations can have a narcotic effect on insects thereby reducing mortality (Winks, 1974a).

Phosphine has an inhibitory effect on insect respiration and is unique in that it is only toxic to insects in the presence of oxygen – in the absence of oxygen it is not absorbed and is not toxic to insects (Bond et al 1967, 1969). However, the action of phosphine is potentiated by carbon dioxide and the exposure time can be reduced when both gases are present (Kashi and Bond, 1975).

Some stages of insects are considerably more tolerant to phosphine than others (Bell, 1976; Hole et al, 1976; Nakokita and Winks, 1981). The eggs and pupae are usually hardest to kill while larvae and adults succumb more easily. Reynolds et al (1967) found that this tolerance was at least partially overcome by the development that occurred in the insects during the relatively long exposure periods. For example, a 10-day exposure of various stages of Sitophilus Granaries was found to be long enough to permit the different stages to reach a susceptible point of development at some time during the fumigation. These results suggest that all pre-adult stages, some of which are quite tolerant to the fumigant, may reach a susceptible stage of development during a 10-day fumigation, so that an exposure period of this length will lead to complete mortality. Howe (1974) discussed problems relating to the laboratory investigation of phosphine toxicity to stored product insects.

Observations to date on the effectiveness of phosphine on mites in bulks of grain indicate that the fumigant may be successful in bringing about immediate reduction in mite populations and thus improving the condition of the grain (Van den Bruel and Bollaerts, 1956). However, populations of some species have been seen to build up again in the grain after an interval of time. This is partially due to the fact that natural predators such as the mite, Chevletus eruditus (Schr.), are eliminated and partially because some stages of destructive species of mites are resistant to the fumigant (Heseltine and Thompson, 1957; Sinha et al, 1967). Tests on dried prunes have shown that satisfactory control of mites on this commodity can be obtained with phosphine (Cangardel and Fleurat-Lessard, 1976).

Insect Resistance

The effectiveness of phosphine can be reduced considerably by development of resistance in insects. Winks (1974b) showed that Tribolium castaneum could develop 10-fold resistance to phosphine in six generations. Resistance may occur in immature stages as well as in adult insects. Bell et al (1977) found a good correlation between resistance in the adult stage of Rhyzopertha dominica and resistance in the egg stage. Champ and Dyte (1976) found evidence of resistance to phosphine in insects from several parts of the world, particularly where inadequate techniques of fumigation were employed, and they indicated that emergence of resistance to fumigants under

practical conditions was a matter of great concern. There is recent evidence (Borah and Chalal, 1979; Tyler et al, 1983) of the development of resistance to phosphine in field populations of Khapra beetle and other insects infesting stored grain. Hole (1981) discussed the variation in tolerance of seven species of stored-product Coleoptera to phosphine in strains from twenty-nine countries. Further information on the nature and occurrence of resistance is given in Chapter 2.

EFFECT ON PLANT LIFE

Seeds

There is considerable evidence from studies so far conducted that phosphine in insecticidal treatments does not, under normal conditions, affect the germination of seeds. Strong and Lindgren (1960b) tested cereal, sorghum and small legume seeds with one or two (repeat) fumigations at comparatively high concentrations. Berstlief and Alexandrescu (1964) confirmed these findings for wheat sod maize under Rumanian conditions and Pinto de Matos (1961) for the germination of groundouts. When a third fumigation was done with phosphine, Fam et al (1974) found no ill effect on the germination of some varieties of tomatoes, sweet melons, cucumbers, peas and beans, but one variety of broad beans was slightly affected. However, the growth and yield of plants grown from seeds subjected to repeated fumigations with phosphine may be significantly reduced. Joubert and Du Toit (1969) reported a reduction in total yield of maize grown from seed fumigated twice sod three times with phosphine.

Living Plants

There is little information on the tolerance of growing plants to the vapours of phosphine. Monro and Upitis (1967) found that 15 varieties of glasshouse plants were tolerant to concentrations which were completely toxic to the postembryonic life stages of the mealybug Plannococcus citri (Risso), but the eggs were not killed. The nematode Meloidopyne hapla may be controlled in potted rose plants with phosphine applied to the soil, without apparent injury to the plants (Faber, 1966).

EFFECT ON PLANT PRODUCTS

Phosphine has been used for many years to control insects in a wide range of plant products throughout the world. To date there has been no report of appreciable adverse effects from recommended treatments.

Mayr and Hild (1966) concluded that normal fumigation with phosphine has no effect on vitamins, particularly vitamins A and B_2 (riboflavin), in a group of important foods which are a regular dietary source of these vitamins. Fumigation of wheat with phosphine under normal conditions has no adverse effect on the baking quality of flour made from it (Neitzert, 1953; Lindgren et al, 1958; Mayr, 1974; Matthews et al, 1970a,b). Phosphine can also be used to control insects (Nelson, 1970; Vincent and Lindgren, 1971) and mites (Cangardel and Fleurat-Lessard, 1976) in dried fruit.

Tests on fresh fruit and vegetables show that insects such as fruit flies can be controlled using gas generated from a magnesium phosphide preparation without injury to the produce. Seo et al (1979) found no injury on papaya, tomato, bell pepper, eggplant or banana fumigated with dosages that eliminated eggs and larvae of the fruit flies Dacus dorsal) Hendl. and Ceratitis capitata Wied. Ten varieties of avocado, although not injured by the treatment, did ripen more quickly than unfumigated avocados. Grapefruit and tomatoes have also been fumigated without injury at concentrations sufficient to kill fruit flies (von Windeguth et al, 1977; Spalding et al, 1978).

The use of phosphine for bulk grain fumigation is described in Chapter 10. Recommended treatments for a number of plant products, including packaged foods, will be found in
Schedule P.

RESIDUES IN FOODSTUFFS

The residues resulting from the use of phosphine fumigants may be of three types: reaction products of the formulation, unchanged phosphine absorbed in commodity or products formed by chemical combination of phosphine with components of the commodity.

Formulations of aluminium or magnesium phosphide leave mainly an inert residue of the metallic hydroxide. In formulations of aluminium phosphide, a small amount of unreacted material may also remain, and hence some precautions should be taken to avoid hazards from the unspent formulation. When processed foods are Fumigated, or when space fumigations are carried out, residue from the formulation should be collected and properly disposed of.

Residue from magnesium phosphide in the plate preparations remains in the plastic matrix in which it is embedded as magnesium hydroxide. The reaction with water vapour is substantially complete, so that no abreacted material remains, and elimination of the residue simply involves collection and disposal of plastic trays at approved sites.

Unchanged phosphine does not remain in fumigated commodities in appreciable amounts. Tolerance levels of 0.1 mg/kg for raw grains and 0.01 mg/kg for processed foods have been established by many agencies and numerous investigations have shown that the gas desorbs rapidly during aeration to levels well below the tolerances (see review by Dietrich et al, 1967). It is interesting to note, however, that minute but detectable traces of phosphine can remain in fumigated commodities for very long periods of time. Dumas (1980) detected phosphine desorbing from fumigated wheat 220 days after the treatment.

Some reaction products may form by combination of phosphine with components of a commodity. Several investigations have shown that small quantities of innocuous

phosphites and phosphates from phosphine remain in fumigated materials (Robinson and Bond, 1970; Disney and Fowler, 1972; Tkachok, 1972; Underwood, 1972).

Recommendation for Tolerances

Taking into account the fact that phosphine aerates rapidly from foodstuffs, and that a residue of 0.1 mg/kg in a raw cereal would yield a much lower residue in bread or other food ready for consumption, the FAD/WHO joint meeting (1967a) considered that there was no necessity to establish a figure for acceptable daily intake. For cereals in international trade a tolerance of 0.1 mg/kg expressed as PH_3 is recommended.

METHODS OF ANALYSIS

Determination of Vapours

For the determination of concentrations of phosphine used in fumigation, glass detector tubes (Figure 18) are available from a number of manufacturers in various ranges from 15 to 3 000 ppm. These tubes, described more fully in Chapter 3, are reasonably reliable, easy to use and are of sufficient accuracy for monitoring approximate concentrations achieved at various stages in a fumigation. For protection of personnel from low levels of phosphine around the threshold limit value (TLV), similar tubes with ranges down to 0.025 ppm can be obtained. A mixed indicator paper strip that will give rapid, sensitive and reliable detection of phosphine around the TLV has been developed by Kashi and Muthu (1975).

Infra-red analysers have been used on an experimental basis for analysis of phosphine and found to have good stability, reproducibility and sensitivity (Webley et al, 1981). The concentration of phosphine is determined by measurement of absorption bands at either 4.2 μm or at 9.0 μm unless carbon dioxide is present; carbon dioxide interferes with analysis of phosphine at 4.2 μm and may need to be absorbed from the sample or the analysis may be done at 9.0 μm. In normal use, sampling can be done by pumping fumigant - air mixture through the analyses but there is also a closed loop injection system for calibration of the instrument or for experimental work. Here small samples can be injected through a septum by a gas syringe. With the infra-red analyses, concentrations up to 2.7 mg/l have been measured under field conditions and, with proper manipulation, levels down to 0.0004 mg/l (0.25 ppm) can be detected.

Gas chromatography has been developed and used extensively for analysis of phosphine in experimental work (Dumas, 1964, 1969; Chakrabarti and Wainman, 1972; Bond et al, 1977). Small, portable gas chromatography suitable for analysing phosphine in commercial treatments are now available on the market. One such instrument that is simple, easy to use and virtually unaffected by air and high moisture levels can measure phosphine below 0.02 ppm (Barker and Leveson, 1950).

Determination of Residues

The problem of determination of residual phosphine in fumigated foodstuffs has been reviewed by Dietrich et al (1967). A sensitive method, developed by Bruce et al (1962) and modified by Sullivan and Murphy (1966) has been widely used for analysis of phosphine residues in many commodities. Kroeller (1968) described a sensitive method with a simplified procedure for plotting the calibration curve using high purity potassium dibydrogen phosphate. These methods are sensitive to less than 0.005 mg/kg.

For analysis of desorbing residual phosphine by gas chromatography the method of Dumas (1978) can be employed.

FORMULATIONS

Both aluminium and magnesium phosphide are manufactured in several different formulations for a variety of applications. Aluminium or magnesium phosphide powder is compressed into hard round or flat tablets about 3 9 in weight or pellets of 0.6 9, which yield approximately 1 and 0.29 of phosphine, respectively. Aluminium phosphide powder is also prepared in permeable paper bags or sachets. Additional materials such as paraffin and ammonium carbamate or ammonium bicarbonate are included in the formulations to regulate moisture uptake and to dilute the phosphine as it is generated. The products are supplied in sealed metal tubes, cans or flasks, which are packed in cases. As long as the containers remain sealed the storage life of the product is virtually unlimited. The pellets and round tablets are supplied in flasks that can be resealed after opening.

For convenience and safety, pellets or sachets are sometimes supplied in predetermined quantities for specific applications. Pellets are prepared in special prepacks of 165 pellets each for treatments such as railway box car fumigations. Similarly, sachets are joined together in ropes or in "blankets". In these prepared packages the pellets or sachets are separated sufficiently to avoid a build up of excessive heat and concentrations of the gas in small spaces.

Magnesium phosphide is also marketed in the form of a flat plate about 280 x 170 x 5 mm and weighing 2069. The active ingredients of the formulation are embedded an inert polyvinyl acetate matrix fabricated in the form of a semi-rigid plate covered on both sides with moisture permeable paper. Every plate is individually sealed in a gas-impermeable foil pouch, or 16 plates interconnected to form a 4 480 mm strip, are similarly sealed in foil and packaged in tins - 32 plates per tin or two strips of 16 plates each.

Once the plates or strips are removed from the foil pouches, they start evolving phosphine within one half to one hour. This formulation is intended to be used for fumigation of bulk goods and packaged and processed commodities. It can be applied successfully under almost nil space storage conditions provided that the structure is tightly sealed. According to the manufacturer, this formulation can also be used to

fumigate fruits and vegetables at recommended dosages without any adverse effects, such as phototoxicity.

The plates and strips provide ease of application and collection after the treatment; there is no danger of contaminating goods with spent fumigant as the plastic matrix retains all such material. Magnesium phosphide formulations release the phosphine more rapidly than aluminium phosphide products, with the maximum gas reading usually being achieved within the first 24 hours.

Magnesium phosphide made in discs weighing 10 9 for control of burrowing rodents and moles is for outdoor use only.

Handling of Phosphine Formulations

Containers of aluminium or magnesium phosphide formulations have labels that give important information concerning use, hazards and precautions. The instructions on the labels should be carefully adhered to during fumigation. Containers should be opened in the open air where any released gas can readily diffuse away. Caution: DO NOT OPEN IN A DUSTLADEN OR EXPLOSIVE ATMOSPHERE. The formulation should be kept away from liquid or water, as this causes immediate release of the gas with possible spontaneous ignition. Also, piling of the formulation or residual dust may cause a temperature increase so that a flash may occur. Gloves should be worn by the person handling the phosphine formulation and smoking or eating should be avoided until the hands are washed after application. Containers with screw type caps are made to be gas-tight and may he resealed if only part of the contents are used. When containers are emptied they should be triple-rinsed with water to remove any traces of abreacted product and then disposed of in an approved disposal site.

APPLICATION

Because phosphine is highly toxic, inhalation of even small quantities of the dust from the formulation, as well as the evolved yes, should be avoided. Pellets or tablets may be applied directly to a grain stream by hand (protected by gloves) or by means of automatic applicators. The rate that the yes evolves from the formulation varies, depending on type of formulation, moisture and temperature. In grain, for example, if the moisture content and temperature are high, all of the gas from aluminium phosphide formulations is evolved within three days. Special probes are used for applying tablets below the surface of bulk grain. Sachets may be applied directly to the grain stream, pushed into the grain bulk or inserted into specially designed, permanently installed pipes in grain bins (Anon, 1980). For some treatments the sachets are laid out in blankets on the surface of grain to allow the gas to evolve and diffuse into the grain mass. Methods of application of phosphine formulations for bulk grain are described and illustrated in Chapter 10.

For the treatment of bagged grains and other raw commodities in transport facilities, such as railway wagons, pellets or tablets may be spread evenly over the load or placed in moisture permeable envelopes to fit in some convenient location near the door before closing. When fumigating packaged commodities under gas-proof sheets the tablets or pellets can be spread out on trays to lay under the sheet before it is secured. In warehouses, after the structure is adequately sealed, the tablets or pellets are spread out on trays or sheets of Kraft paper so that residual material can be easily collected at the end of the treatment. The tablets or pellets should never be piled on top of each other or in a mass.

On completion of the fumigation, all windows and doors should be opened and the space aerated for at least two hours. A gas reading should be taken with a suitable analyses before entering the fumigated area. If it is necessary to enter the fumigated space to open doors and windows a gas mask with a canister designed for phosphine must be worn.

Disposal of Spent Reaction Products

After a fumigation, any residual material left from the reaction process should be disposed of in an approved manner. This can be accomplished by burying or by slowly adding the dust to a container of water (with detergent as a wetting agent) and stirring into the water until a slurry is formed and the residue sinks. If prepacks have been used the entire strip should be submerged in the water-detergent mixture and allowed to soak for 36 hours before disposal. For purposes of safety the disposal procedure should be carried out in the open air, where any generated phosphine can rapidly disperse.

Spent plates or prepacked strips may be held out of doors in locked wire containers and moved to an approved disposal site at monthly intervals, or whenever the container is full.

In fumigation treatments of raw agricultural commodities such as grain or bulk animal feeds, no special disposal procedures are needed because any of the phosphide formulation that may remain is further decomposed and removed along with grain dust in the handling and turning that accompanies further processing of the grain (liscombe, 1963).

PRECAUTIONS

Reaction with Metals

Phosphine is practically insoluble in water, fats anti oil and is stable at normal fumigation temperatures so that it has no appreciable reaction with most fumigated commodities. It may, however, react with certain metals, particularly copper, copper compounds, silver and gold to cause corrosion. This reaction is enhanced by the presence of ammonia, which is given off during the decomposition of some proprietary formulations. High humidity and temperature appear to favour the reaction, particularly in air with a salt content as found near the sea.

As a result of this reaction any copper-containing equipment, especially electrical apparatus, may be severely damaged. During fumigation of buildings with phosphine special attention should be given to electric motors, electric wiring, switches, fire alarm systems, electronic systems or other pieces of equipment that contain copper (Bond et al, 1984).

If equipment that is liable to damage cannot be removed from the area being treated some protection may be afforded by coating copper materials with a thin layer of paraffin, spraying with a light lubricating oil or using techniques that will keep the concentration of phosphine and the humidity low.

Concentrations Toxic to Humans

The threshold limit value-time weighted average (TLV-TWA) for an eight hour daily exposure in a five-day week is set at 0.3 ppm (ACGIH, 1981). The maximum concentration to which workers should be exposed for a period up to 15 minutes is 1 ppm, with the stipulation that at least 60 minutes should elapse between such exposures and provided the daily TLV-TWA of 0.3 ppm is not exceeded.

Should a person become exposed to phosphine as a result of inattention, negligence, failure to follow proper procedures or some other reason and, as a result, symptoms consisting of fatigue, ringing in the ears, nausea, or pressure in the chest appear, he should go immediately into the open fresh air. Symptoms of poisoning by a small quantity of phosphine will normally disappear when a person is removed to the fresh air. However, despite the seeming insignificance of even mild cases of poisoning with symptoms as described above, first aid measures (see below) are absolutely imperative before and until the arrival of a doctor.

Under no conditions should an affected person resume work during the next 48 hours, particularly work dealing with fumigation, as it takes time for the body to eliminate the poison completely. Complete abstinence from alcoholic beverages after any poisoning is strongly recommended.

Respiratory Protection

For personal protection against the vapours of phosphine at concentrations above the threshold limit, a respirator, gas blouse or other similar equipment for supplying uncontaminated air must be used. Respirators with a special canister for phosphine vapours will give protection up to 0.5 percent phosphine by volume in air (Kloos et al, 1966). Above this concentration, air must be supplied by an air-line or self-contained breathing equipment. Appropriate detection equipment for measuring concentrations of phosphine in air should be used in conjunction with respiratory protective devices to ensure adequate protection.

General Precautions

Full precautionary instructions are supplied by the manufacturers of the proprietary materials used for generating phosphine. Some of the more important precautions are listed here.

1. Gloves should be worn when tablets or pellets are being dispensed by hand.

2. Respirators need not be worn when tablets or pellets are being dispensed under conditions where the operator does not breathe the vapours of phosphine. Under normal conditions, there is a delay in evolution of the fumigant from the formulations described in this manual. Respirators equipped with a canister designed for protection against phosphine (see above) or other appropriate respiratory equipment should always be on hand in case of emergency.

3. Odour of the fumigant cannot be relied upon as an indication of whether or not the operator is breathing poisonous concentrations. Detection equipment such as glass detector tubes or other detectors should be used to monitor concentrations of the gas and to determine when an area is free of fumigant after a treatment.

4. Do not smoke or touch food at any time during the application of this insecticide.

5. Any spaces adjoining silo bins or close to other structures undergoing treatment with phosphine should be kept continuously aired by leaving windows open or by providing artificial ventilation by means of fans or blowers.

6. All persons working, or likely to work, in any place near the fumigation area must be notified that fumigation is in progress. Warning notices should be posted to prevent exposure of employees or the public at large to the gas.

7. When the fumigation is completed and the grain is turned, or aeration of a structure is undertaken, full precautions must be undertaken to ensure that no person is exposed to residual vapours of the fumigant.

FIRST AID

Symptoms of Poisoning

According to the amount of phosphine inhaled, symptoms may occur immediately or several hours after exposure.

Slight or mild poisoning may give a feeling of fatigue, ringing in the ears, nausea, pressure in the chest and uneasiness. All of these symptoms will normally disappear in fresh air.

Greater quantities will quickly lead to general fatigue, nausea, gastrointestinal symptoms with vomiting, stomach ache, diarrhoea, disturbance of equilibrium, strong pains in the chest and dyspnoea (difficulty in breathing).

Very high concentrations rapidly result in strong dyspnoea, cyanosis (bluish-purple skin colour), agitation, ataxia (difficulty in walking or reaching), anoxia (subnormal blood oxygen content), unconsciousness and death. Death can be immediate or occur several days later due to oedema and collapse of the lungs, paralysis of the respiratory system or oedema of the brain. Disturbances of kidney and liver functions (hematuria, proteinuria, uraemia, jaundice) and cardiac arrhythmia may occur.

Advice to the Physician

The following measures are suggested by the manufacturer for use by the physician in accordance with his own judgement.

In its milder forms, symptoms of poisoning may take some time (up to 24 hours) to make their appearance, and the following measures are suggested:

1. Complete rest for one or two days, during which the patient is kept quiet and warm.

2. Should the patient suffer from vomiting or increased blood sugar, appropriate intravenous solutions should be administered. Treatment with oxygen breathing equipment is recommended as is the administration of cardiac and circulatory stimulants.

In cases of severe poisoning intensive care in a hospital is recommended:

1. Where pulmonary oedema is observed, steroid therapy should be considered and close medical supervision is recommended. Blood transfusions may be necessary.

2. In case of manifest pulmonary oedema, venesection should be performed under vein pressure control, and intravenous administration of glycosides (in case of hemoconcentration, venesection may result in shock). On progressive oedema of the lungs, perform immediate incubation with constant removal of oedema fluid and establishment of oxygen positive pressure respiration, as well as any measures required for shock treatment. In Case of kidney failure, extracorporeal haemodialysis is necessary. There is no specific antidote known for this poison.

3. Suicide may be attempted by taking solid phosphides by mouth. In such a case, empty the stomach by inducing vomiting and flush it with a dilute potassium permanganate solution or a solution of magnesium peroxide until the flushing liquid ceases to smell of carbide. Thereafter, administer medicinal charcoal.

4. Scientific research has shown that phosphine poisoning is not chronic; the action of phosphine is reversible and symptoms will disappear by themselves.

HYDROGEN CYANIDE (HCN)

Hydrogen cyanide was one of the first fumigants to be used extensively under modern conditions. Its use for treating trees under tents against scale insects was developed in California in 1886 (Woglum, 1949). The use of HCN has been declining in recent years, but it is still important in certain fields of application.

HCN is one of the most toxic of insect fumigants. The fact that it is very soluble in water has considerable bearing on its use in practice. Thus, it may produce injury on moist materials, such as fruit and vegetables, because the solution of HCN in water is a dilute acid. Not only does this acid render these materials unpalatable and possibly hazardous for human consumption, but its action, by causing burning, wilting or discoloration, may make them unmarketable.

On the other hand, HCN has been widely used for fumigating dormant nursery stock that is sufficiently dry. It may be used for some living plants if they can be washed with water immediately after treatment to prevent burning by the acid.

HCN may be employed for fumigating many dry foodstuffs, grains and seeds. Although HCN is strongly sorbed by many materials, this action is usually reversible when they are dry, and, given time, all the fumigant vapours are desorbed. With many foodstuffs little, if any, chemical reaction occurs, and there is no detectable permanent residue.

Because of the high degree of sorption at atmospheric pressure, HCN does not penetrate well into some materials. It WAS largely because of this that vacuum fumigation was adopted.

TOXICITY

HCN is a powerful, quick acting poison. In humans and other warm-blooded animals it induces asphyxiation by inhibiting the respiratory enzymes and renders tissues unable to absorb oxygen from the blood in the normal manner. The toxic action is reversible. In practice, this means that a person who is completely unconscious from the effects of cyanide, but whose heart is still beating, may still recover if suitable antidotes nod remedial measures are applied in time. HCN may be absorbed in toxic amounts through the unbroken skin (see below under "Precautions").

Toxicity of Residues

After ingestion by mammals, HCN is rapidly converted into thiocyanate (Lehmann, 1959), which is far less toxic. In a carefully controlled laboratory experiment conducted during a period of two years, rats were fed a regular diet containing 100 or 300 ppm by weight of HCN. The rats were reared on this diet from the weaning stage and during growth or maturity they did not exhibit any symptoms of poisoning. Growth and development were the same as in the controls (Howard and Hanzal, 1955). These results indicate that residues of HCN in fumigated foods, which would normally

be far less than the amounts used in these tests, would be of no hazard to human consumers. The effect of HCN on specific types of foodstuffs is discussed under "effect on Plant Products".

PROPERITES OF HYDROGEN CYANIDE

Alternative name : hydrocyanic acid; abbreviation used : HCN

ODOUR	Suggestive of almonds
CHEMICAL FORMULA	HCN
BOILING POINT	26°C
FREEZING POINT	-14°C
MOLECULAR WEIGHT	27.03
SPECIFIC GRAVITY GAS (AIR = 1)	0.9
LIQUID (WATER AT 4°C = 1)	0.688 at 20°C
LATENT HEAT OF VAPORIZATION	210 cal/g
FLAMMABILITY LIMITS IN AIR	6 to 41% by volume
SOLUBILITY IN WATER	Infinite at all temperatures
PERTINENT CHEMICAL PROPERTIES	Weak acid. Relatively noncorrosive. When stored as a liquid without chemical stabilizer may decompose and explode in the container.
METHOD OF EVOLUTION AS FUMIGANT	Discharge from steel cylinder with aid of compressed air. By evaporation of liquid absorbed in porous material, such as card board discs or diatomaceous earth. By action of moisture in air on calcium cyanide, or of sulphuric acid on sodium cyanide
COMMERCIAL PURITY	96 to 99%

Natural vapour pressure at different temperatures

0°C (32°F) 264.3 mm Hg
10°C (50°F) 400.0 mm Hg
20°C (68°F) 610.0 mm Hg
25°C (77°F) 738.8 mm Hg
30°C (86°F) 910.0 mm Hg
40°C (104°F) 1 269.2 mm Hg

Weights and volumes of liquid

1 lb (avdp) at 20°C has volume 659.7 ml
1 U.S. gal weighs 5.82 lb (2.643 kg)
1 Imp gal weighs 6.99 lb (3.171 kg)
1 kg has volume 1 454.3 ml
1 litre weighs 0.688 kg

Dosages and concentrations of gas in air (25°C AND 760 MM PRESSURE)

BY VOLUME		WEIGHT PER VOLUME	
PARTS PER MILLION	PERCENT	[1]G/M³	LB/L 000 FT³
[2]10	0.001	0.011	
50	0.005	0.055	
100	0.01	0.11	
200	0.02	0.22	
500	0.05	0.55	0.03
905	0.09	1.00	
1 000	0.10	1.105	0.07
14 473	1.44	16.00	1.00
20 000	2.0	22.11	1.38

[1] Ounces per 1000 cubic feet or milligrams per litre
[2] Threshold limit (ACGIH, 1981).

Toxicity to Insects

Among the commonly used fumigants, HCN is one of the most toxic to insects. It also has a rapid paralysing effect on most species. This action is an important consideration in dealing with insects, because sublethal concentrations may bring about apparent death. After exposure to the fumigant, the reversible action of the poison may permit the insect to recover. This reaction has already been referred to as protective stupefaction (Lindgren, 1938). It is important from the practical point of view because it means that the maximum recommended concentration should be attained as quickly as possible during the application of the fumigant.

FLAMMABILITY

The flammability limits of HCN in air lie between 6 and 41 percent by volume. These limits are well above the normally recommended fumigation doses of up to 1.5 percent (16 g/m^3 or 16 $oz/l\ 000\ ft^3$). However, it must be pointed out that, at the point of release of the gas at the beginning of a fumigation, a concentration within these limits

may exist for a short length of time. If there is any flame (such as a pilot light) or sparks near temporary high concentrations, a serious fire or explosion could occur. In working with this fumigant, great care must be exercised to extinguish all flames and turn of all electric switches before a treatment begins.

EFFECT ON PLANT LIFE

Seeds

HCN applied in dosages effective against insects does not affect the viability of seeds that are normally dry, with moisture contents suitable for storage. In a comprehensive study, the results of which were published between 1959 and 1961, Strong and Lindgren studied the effect of HCN in insecticidal concentrations on the germination of a wide range of seeds, including grain seeds, flax and small legumes. The variable factors considered were moisture content (8 to 14 percent), repeat fumigations and post fumigation storage. It was concluded that germination of wheat, barley, oats, rice and flax seeds was not impaired by one or two fumigations with HCN. With the small legumes with a range of 5.8 to 12.2 percent moisture content (Ranger alfalfa, alsike clover, Ladino clover, Kenland red clever and Viking birdsfoot trefoil), all were tolerant to HCN in one or two fumigations, except aisike clover for which there was positive indication of impairment of germination.

Among 80 varieties of grain, vegetable and flower seeds tested by Lindgren et al (1955), six showed evidence of reduced germination. These were pole beans, burnet, California black mustard, smilo, marigold and snapdragon.

It may be concluded that HCN is a safe fumigant to use for seed treatment, especially for cereal grains under normal conditions, but with flower and vegetable seeds preliminary trials with local varieties are advisable.

Growing Plants and Trees

A considerable amount of injury, either temporary or permanent, may be sustained by actively growing plants fumigated with HCN. Because this gas is very soluble in water, special precautions have to be taken to reduce the amount of moisture on leaves and stems and in pots or soil balls of actively growing plants. Therefore, the plants should not be watered for one or more days before treatment. After treatment with HCN, it is necessary to wash the plants with water to remove any residual acid. HCN interferes with photosynthesis and other physiological processes (Moore and Willaman, 1917); for that reason, plants may be more susceptible to injury in daylight. Usually, treatments have to be carried out at night or in the dark. Also, following exposure, plants should be kept away from sunlight for several hours.

In the past HCN was widely used for fumigating ornamental and glasshouse plants, but it has been replaced by other fumigants that are less phytotoxic. The use of HCN generated from calcium cyanide to control glasshouse pests is discussed in Chapter

12. HCN was extensively used for may years to control scale insects on citrus trees in a tent fumigation procedure (Quayle, 1938). In this treatment, HCN gas (5 g/m) from liquid HCN, or evolved from a salt such as calcium cyanide, was liberated into a relatively gas-tight tent installed over the tree and maintained for usually around 45 minutes. A number of factors, including temperature, humidity, physiological conditions of the tree (such as dormancy, disease, cultural conditions, stage of development and others), have considerable influence on the tolerance of the trees to the fumigant (Woglum, 1923). Since different species or varieties of citrus trees show wide variation in response and the insects in different areas may vary in tolerance, the actual conditions of treatment usually have to be developed to suit local circumstances. In scale insect eradication work, where complete kill of all insects is essential, the tent fumigation treatment with HCN has been found to be a valuable technique (Fosen et al, 1953). HCN was used by Del Rivero et al, (1974) to control larvae and eggs of the woolly white fly on orange trees.

While the concentrations of HCN required to kill insects may cause severe injury to growing plants, lower concentrations of HCN may stimulate growth and be useful in "forcing" growth in some species (Gassner, 1925).

Dormant Nursery Stock

HCN is still used in many parts of the world for the fumigation of the dormant nursery stock of deciduous trees, especially in quarantine treatments against the spread of scale insects (Ceder and Mathys, 1949; van de Pol and Rauws, 1957; Agarwala, 1956; Jen and Lai, 1959). As in growing plants, a marked stimulation has been noticed in some nursery stock fumigated with HCN (Cassner, 1925). Immediately following fumigation it is sometimes necessary to wash plants with water to avoid the burning of buds and new foliage.

EFFECT ON FOODSTUFFS

For the most part, HCN does not react with the constituents of foodstuffs of normal moisture content. For example, materials such as honey and beeswax that have been exposed to HCN in treatments designed to destroy the bee colonies at the end of a season, were found to have less than 0.004 and 0.02 mg/kg CN (Ihnat and Nelson, 1979). Important exceptions or special considerations are noted in the paragraphs below.

Fresh Fruit and Vegetables

HCN is not generally recommended for the fumigation of fresh fruit and vegetables. It is used to some extent in the treatment of citrus and other fruit for the control of scale insect or thrips (Richardson and Balock, 1959). In some countries HCN is used in quarantine treatments of bananas, pineapple and other commodities for the control of aphids, mealy bugs and other exposed insects (Figure 19). The European Plant Protection Organization recommends HCN in a vacuum treatment for bulbs, rhizomes,

tubers, asparagus roots and strawberry plants to control certain mites and nematodes (EPPO, 1976).

Cereals and Milled Foods

HCN has been used safely and successfully against a wide range of dry plant products used as foods. An interesting exception to the general rule is that some HCN is retained by fumigated bran in combined form, hut this residue has no adverse effect on mixed feed containing average amounts of the treated bran (Page and Lubatti, 1948). At atmospheric pressure, it does not penetrate as quickly or as effectively as dues methyl bromide. This handicap can be overcome in bulk grain fumigations by the use of recirculating systems. Kunz et al (1964) studied the penetration of HCN through a mass of grain sorghum. The variables of temperature, moisture and dockage all reduced penetration in proportion to their increase.

Dried Fruit

Although HCN has been used for many years in the treatment of dried fruit, this practice is safe only under carefully controlled conditions. HCN may react with laevulose to form laevulose cyanohydrin, a poisonous compound that is fairly stable (Page and Lubatti, 1948). The amount of cyanohydrin formed in dried fruit varies with its moisture content and this should be kept to a minimum during fumigation. With properly conducted treatments at normally recommended dosages and exposure periods, the small amounts of residues that may form would not present a danger. In one instance, careless application of the fumigant permitted liquid HCN to run into packages of dried fruit and an outbreak of food poisoning ensued from the excessive residues of hydrocyanic acid present at the time of consumption (American public Health Association, 1938).

METHODS OF ANALYSIS

Determination of Vapours

Various devices are available for determining whether a space fumigated with HCN is sufficiently aerated to permit human entry or whether a given material is adequately free of gas to allow handling. An important use of these devices is for testing bedding and clothing after fumigation in order to discover whether HCN is sufficiently desorbed so that warmth from the body may not release dangerous concentrations of the gas. All "handy" devices for indicating fumigant concentrations should be used with care. Instructions for their use should be followed meticulously. Judgement is required for the proper interpretation of the readings, and this improves with experience.

Test papers. Specially prepared test papers have been used successfully as indicators of the presence of HCN in dangerous concentrations. At present, two kinds are in general use, referred to respectively as methyl orange and benzidine copper acetate test papers.

Filter papers dipped in a solution containing methyl orange and mercuric chloride give reliable indications only down to 25 ppm of HCN in air at temperatures above 10°C. However, if kept moist in a tightly stoppered bottle away from light, the papers will be in a fit condition for practical use for up to three months after preparation. The reaction of the papers is slow. In the presence of HCN they turn from an orange colour to various shades of pink, the usual period of exposure being two minutes (Sherrard, 1928). It is unnecessary for the observer to Stay in the space being tested; often the papers may be lowered into a space on a string or held through a door or window on the end of a stick.

The papers made from a solution containing benzidine acetate and copper acetate are sensitive to 10 ppm of HCN in air (Brown, 1952). The change in colour from white to various shades of blue, according to the concentration of HCN, takes place in ten seconds, and it is usually necessary for the operator to make the reading in the contaminated atmosphere. These papers have to be dipped in the mixture of solutions immediately before the test is made. Also, because the mixture is very unstable, the two solutions must be kept separate and only mixed shortly before use. The benzidine acetate solution itself is unstable and must be kept away from light in a brown bottle. Since benzidine compounds are known to have carcinogenic potential, appropriate precautions should be taken if this test method is used.

Manufacturers or suppliers of various types of cyanide fumigants give full instructions for making and using test papers. Some manufacturers also supply the methyl orange test papers ready for use and others have special test kits available for making the benzidine copper acetate papers on the job.

Automatic toxic gas detector. A portable, fully automatic detector based on the colour stain formed by reaction of the gas with reagents in a chemically impregnated paper is available for measuring hydrogen cyanide at TLV levels (J. and S. Sieger Ltd., Poole, Dorset. U.K.). This instrument provides in a rugged, lightweight unit, a sampling pump, sampling head and a simple photopic system for direct reading of the gas concentrations. By changing the sampling period and/or the electronic gain, a whole range of concentrations can be analysed. Tapes are available from the manufacturer for a number of different toxic gases.

Glass detector tubes. A number of glass detector tubes are available on the market for detection and measurement of HCN. Low range tubes that give concentration readings from 1 - 50 ppm can be used for health protection purposes and high range tubes designed to measure the levels used in fumigation treatments (0.05 to 2.0 percent) are available. (For calculations on conversion of concentration values from ppm or percent to g/m , see Chapter 2).

Chemical analysis. A simple method for determining HCN concentrations during fumigation is the silver nitrate method of Liebig, with modifications (supples, 1933). Samples of air/gas mixture are removed by aspiration and the HCN is absorbed in 2

percent sodium hydroxide solution. Titration is carried out with a standardized silver nitrate solution in the presence of potassium iodide.

White (1948) described a simple field method based upon the established phenolphthalein test for HCN. The air/gas sample drawn from the fumigation system is scrubbed through a trisodium phosphate solution containing phenolphthalein and copper sulphate and the fumigant concentration is measured calorimetrically.

The use of the thermal conductivity analyser with this fumigant is not recommended by Heseltine (1961) because of a number of technical difficulties involved.

Laboratory analysis. HCN can be measured over a range of concentrations by gas chromatography (Berck, 1965a; Donike, 1973, 1974; Darr et al, 19980).

Determination of Residues

A number of methods have been developed for the determination of residual HCN in foodstuffs. These are based on the original work of Lubatti (1935) on the analysis of cereals for this compound.

A satisfactory procedure for this analysis is given by the U.S. Food and Drug Administration (1964). Ihnat and Nelson (1979) described a method for determining cyanide residue levels in extracted honey, comb honey and wax cappings, and Toothill (1974) outlined a method for cyanide residues in grain.

APPLICATION

HCN is generated and applied in several different ways; the choice of method depends on convenience, cost and the type of structure or material being treated.

Generation by Acid on Salt

HCN for fumigation was first generated by the action of an acid on a cyanide. Although largely replaced by other more convenient techniques, this reaction is still popular for certain purposes because it is economical and lends itself to emergency treatments. Both potassium cyanide, KCN, and sodium cyanide, NaCN, may be used. Sodium cyanide is cheaper and is the salt used principally today. Sodium cyanide for fumigation should contain not less than 96 percent NaCN and is best purchased in moulds (sometimes egg shaped) each weighing an amount convenient for measuring dosages. Sulphuric acid, H2S04, is the only commercial acid which gives a good reaction without undesirable side effects. It should be purchased in the commercially pure form at 66° Beaume' (specific gravity 1.84).

The procedure for generating HCN for fumigation from sodium cyanide and sulphuric acid in crocks, barrels or special generators is discussed in Chapter 8.

Generation from Calcium Cyanide

Calcium cyanide, Ca (CN)2, is a dark grey powder which yields HCN in reaction with the moisture in the air. The material is marketed, sometimes with a carrier, in different degrees of fineness of the granulations according to the intended use. For example, a fine grade is used for blowing small amounts into ants' nests with a hand duster. Larger granules are used for application to soil, for spreading on the floors of glasshouses or for mixing with grain. The amount of gaseous HCN yielded is between 25 and 50 percent of a given weight of granular material.

Volatilization of Liquid HCN

HCN may be purchased in cylinders as a liquid of 96 to 98 percent purity. The liquid contains a stabilizer which extends the storage life of the fumigant by inhibiting its tendency to generate heat during decomposition and to explode. Nevertheless, the manufacturers place a limit on the length of time a given lot may be kept, usually six months, after which the cylinder must be returned to the factory. This time limit should be strictly adhered to.

At normal temperatures, the natural vapour pressure of the fumigant is not sufficient to propel it into the open, especially when the liquid has to flow through piping. It is necessary to apply compressed air above the surface of the liquid to force it through the siphon tube out of the cylinder (Figure 20).

In vacuum fumigation, the reduced pressure in the chamber is sufficient to draw the liquid HCN from the cylinder. The discharge tube should pass through a heat exchanger en route to the vacuum chamber, as rapid volatilization of the fumigant brings about loss of heat with the possibility of freezing in the lines and tubes. The USE of the liquid in cylinders is a more expensive method of dispensing the fumigant but, in large-scale operations, it is much safer and more convenient to handle HCN in this form and lengthy postfumigation cleaning is eliminated.

Absorption in Carriers

HCN may be purchased absorbed in inert materials. A convenient method of absorption is the use of highly porous cardboard discs. They are shipped in carefully sealed tin cans that withstand the pressure exerted by the absorbed fumigant at the highest temperatures normally encountered. Before the cans are opened, it is advisable to pre-cool them in cold water, ice, or in a refrigerator at 0°C. They are opened with special can openers (Figure 21) supplied by the manufacturers, and the discs are scattered in the space to be fumigated according to the required dosage. It is necessary that proper respirators be worn by those opening the cans and distributing the discs.

The discs are sometimes marketed with 2 to 5 percent chloropicrin used as a warning agent. Small amounts of ethyl bromoacetate have also been used for this purpose.

Disposal of Used Fumigant

In some countries the HCN remaining in an atmosphere after a fumigation must be absorbed and degraded or otherwise safely disposed of. A method and apparatus for decomposition of HCN to non-toxic compounds is given by Hatakoshi (1976).

PRECAUTIONS

Respirators

Respirators fitted with the canister for acid gases will give protection against HCN and must be worn during all operations in which there is exposure to any concentration of this gas.

Absorption Through Human Skin

HCN may be absorbed in toxic amounts through the unbroken skin; the amount is increased if the skin is moist. With modern fumigation techniques it is unnecessary for an operator to remain in a full fumigation concentration of HCN. The fumigant is either discharged from cylinders outside the structure or the gas is generated indoors by one of the methods described above. In the second type of operation, workers who apply granular calcium cyanide or HCN discs, or who initiate generation by dropping sodium cyanide into acid, are able to move away before a heavy concentration of fumigant builds up. During the aeration process it is usually possible to open some doors and windows from outside the structure and to start exhaust fans and blowers so that the full concentration of HCN in the air may be reduced before any person goes inside.

Although the industrial-type respirator canister will remove concentrations of HCN in air up to 2 percent by volume for a limited length of time, it is recommended, in order to avoid absorption of dangerous amounts through the skin, that persons wearing respirators do not remain for more than 5 minutes in concentrations of 0.75 percent or for more than 20 minutes in concentrations of 0.5 percent.

Symptoms of Poisoning

Unless a person is immediately overcome by an overpowering concentration of HCN, a situation unlikely to be encountered in fumigation work when proper precautions are taken, there are preliminary symptoms which serve as a warning of poisoning. These symptoms are common to poisoning caused both by breathing HCN or by its absorption through the skin. More common warning symptoms are:

- irritation of the mucous membrane of the eyes, throat and upper respiratory tract;

- burning sensation on the tongue;

- metallic taste in the mouth

- feeling of pressure in the forehead;

- sharp pains in the head;

- giddiness and disturbed equilibrium;

- nausea and vomiting

If any of the foregoing, or related symptoms are experienced while a person is in the presence of HCN in any concentration, he should move immediately into fresh air, preferably where it is warm, and, if necessary, undergo the first aid treatment outlined below.

The concentrations of HCN that may bring about toxic effects if inhaled by humans are summarized in Table 12.

Although the poisonous action of HCN is rapid, a person may live for several hours after being completely overcome (Chen et al, 1935). Thus, even if there is some delay in the application of remedial treatments by the physician, it may still be possible to bring about the recovery of the patient.

TABLE 12. - POSSIBLE TOXIC EFFECTS TO HUMANS FROM INHALING HYDROGEN CYANIDE (HCN)

HCN CONCENTRATION IN AIR		POSSIBLE EFFECTS ON HUMANS IF GAS IS INHALED
PARTS PER MILLION	G/M^3 ($OZ/1\ 000\ FT^3$)	
10	0.011	Threshold limit for continuous daily exposure of 8 hours.
25	0.027	Slight symptoms after several hours breathing. May lead to chronic poisoning.
50	0.055	Serious disturbances after breathing 0.5 to 1 hour.
100	0.11	Dangerous after breathing 0.5 to 1 hour with possible fatal results.
200	0.22	Quickly kills human beings and other mammals.

FIRST AID

The following items, especially designed to combat HCN poisoning, should be included in the first aid kit:

- 12 pearls amyl nitrite;
- 2 ampoules of sodium nitrite (10 $cm^3$of 3 percent solution);
- 2 ampoules of sodium thiosulphate (50 $cm^3$of 25 percent solution);
- 1 sterile syringe, 10 cm^3;
- 1 sterile syringe, 50 cm^3;

This kit must be on hand every time HCN is used. The amyl nitrite is the only item which may be administered by the fumigators themselves; the others are for the use of a physician only.

The following procedure and instructions for administration of antidotes are based on the recommendations of a manufacturer of HCN fumigants (American Cyanamid Company, 1962).

Poisoning by the gas may not be fatal if prompt action is taken. Do not rush an unconscious person to the hospital. Prompt action on the spot is essential.

1. Do not breathe gas yourself even for a short time. If it does not overcome you, it will cut down your strength. Rescuers entering a contaminated area must be adequately protected with self-contained breathing apparatus and any necessary protective clothing. Canister type gas masks are not dependable under such circumstances of possible high concentration.

2. Carry patient to fresh air, and lay him down. Fresh air does not mean out of doors in cold weather. Many persons have walked from a warm room containing gas only to collapse in the cold outside air. Take the patient to a comfortably warm room free of gas. Remove contaminated clothing but keep patient warm. Start following first aid treatment immediately and call a physician.

3. Break an amyl nitrite pearl in a cloth and hold lightly under the patient's nose for 15 seconds. Repeat five times at about 15-second intervals. Use artificial respiration if breathing has stopped.

4. Never give anything by mouth to an unconscious person.

Suggested Care by a Physician

Antidotes should be administered by a physician only and the following method of administration is suggested.

1. The physician will decide on further administration of amyl nitrite. He will quickly load his syringes, one with 10 $cm^3$of a 3 percent solution of sodium nitrite and the other with 50 cm of a 25 percent solution of sodium thiosulphate. Only the specially prepared intravenous solutions in ampoules should be used.

2. Stop administration of amyl nitrite and inject intravenously 0.3 9 (10 cm of a 3 percent solution) of sodium nitrite at the rate of 2.5 to 5 cm^3per minute.

3. Inject by the same needle and vein, or by a larger needle and a new vein, 12.5 g (50 cm of a 25 percent solution) of sodium chiosulphate.

The patient should be watched for at least 24 to 48 hours. If signs of poisoning reappear, injection of both sodium nitrite and sodium thiosulphate should be repeated, but each in one half of the previous dose.

Even if the patient looks perfectly well, the medication may be given for prophylactic purposes two hours after the first injections.

If respiration has ceased but the pulse is palpable, artificial respiration should be applied at once. The purpose is not only to revive the respiration per se, but also to keep the heart beating. A handkerchief containing amyl nitrite should be laid over the patient's nose, for it may hasten the resumption of respiratory movements. When signs of breathing appear, injection of the above solutions should be made promptly.

Artificial Respiration

Artificial respiration by the traditional Schafer (prone pressure) method is no longer accepted as adequate. When breathing stops, artificial respiration should be given at once by an effective method. The Holger Nielson method is to be preferred and it is recommended that fumigation crews be trained in this. Although mouth to mouth resuscitation is the most effective technique for an emergency, it may be difficult to apply if the patient is being administered amyl nitrite. Furthermore, there may be danger to the rescuer himself if the patient is highly contaminated with HCN in or on the mouth or in the region of the face.

ETHYLENE DIBROMIDE

The insecticidal properties of ethylene dibromide (EDB) were reported by Neifert et al in 1925. It has become important as an insecticidal fumigant as a result of its specific value for the destruction of fruit flies (family Trypetidae) in fruit (Viel and Catelot-Goldman, 1957) and as a fumigant for grain in the tropics. It has also been found useful throughout the world as an ingredient of a number of liquid-type grain fumigants and "spot" fumigants. The role of EDB in fumigant mixtures will be discussed in Chapter 7.

Although EDB is a fumigant of considerable utility, it has a high boiling point and is sorbed by many materials, into which it does not penetrate well. It is thus more limited in usefulness than some of the more volatile fumigants. It has, however, found extensive use in soil fumigation, a subject outside the scope of this manual. It is also effective as an ingredient in very low proportions of dips to control fruit flies in fruit (Cohen and Nadel, 1958; Wolfenbarger, 1962; and Burditt et al 1963). In this use, the insecticidal effect is undoubtedly due to fumigant action.

TOXICITY

Ethylene dibromide is more toxic to human beings than methyl bromide. It is a severe skin irritant and can be absorbed through the skin as well as the respiratory tract. High concentrations can affect the lungs and injure liver and kidneys (Torkelson et al, 1966). When fed in small amounts to laying hens in fumigated grain, EDB was found to decrease the size and number of eggs (Bond) et al, 1955; Caylor and Laurent, 1960). In bulls, malformations of sperm cells appeared in the semen (Amir and Volcani, 1967). In addition, EDB has been investigated for its carcinogenic effects and shown to be capable of producing cancer in laboratory animals (Olson et al, 1973). Chemicals found to be carcinogenic in animal tests are generally considered, by the U.S. National Cancer Institute, to be a potential threat to human health (U.S. Department of Heath, Education and Welfare, 1979). Therefore, appropriate precautions should be taken to avoid exposure to this fumigant.

A serious toxic interaction between inhaled EDB and ingested disulphiram (tetraethylthiuram disulphide) has been demonstrated in experimental animals (Stein et

al, 1978). Furthermore, Plotnick (1978) found that disulphiram in the diet of rats exposed to a low level of EDB (20 ppm) increased the incidence of tumours. As disulphiram is used in therapy for alcoholism, as well as in certain industrial processes, special precautions against possible exposure to the two chemicals together are indicated.

PROPERITES OF ETHYLENE DIBROMIDE
ALTERNATIVE NAMES : 1, 2-DIBROMOETHANE, ETHYLENE BROMIDE
ABBREVIATION USED IN THIS MANUAL : EDB

ODOUR	Like chloroform
CHEMICAL FORMULA	$CH_2Br.CH_2Br$
BOILING POINT	131.6°C
FREEZING POINT	10 C
MOLECULAR WEIGHT	187.88
SPECIFIC GRAVITY	
GAS (AIR = 1)	6.487
LIQUID (WATER AT 4°C = 1)	2.172 at 20°C
LATENT HEAT OF VAPORIZATION	46.2 cal/g
FLAMMABILITY LIMITS IN AIR	Non-flammable
SOLUBILITY IN WATER	0.431 g/100 ml at 30°C
PERTINENT CHEMICAL PROPERTIES	Stable
METHOD OF EVOLUTION AS FUMIGANT	By evaporation of liquid, often in mixture with other fumigants

Natural vapour pressure at different temperatures

0°C (32°F) 3.5 mm Hg
10°C (50°F) 6.0 mm Hg
20°C (68°F) 11.0 mm Hg
25°C (77°F) 14.0 mm Hg
30°C (86°F) 17.5 mm Hg
40°C (104°F) 28.5 mm Hg

Weights and volumes of liquid

1 lb (avdp) at 25°C has volume 208.8 ml
1 U.S. gal weighs 18.11 lb (8.215 kg)
1 Imp gal weighs 21.72 lb (9.852 kg)

1 kg has volume 460.4 ml
1 litre weighs 2.172 kg

Dosages and concentrations of gas in air (25°C AND 760 MM PRESSURE)

BY VOLUME		WEIGHT PER VOLUME	
PARTS PER MILLION	PERCENT	[1]G/M³	LB/L 000 FT³
25	0.0025	0.19	
50	0.005	0.38	
100	0.01	0.77	
130	0.013	1.00	
200	0.02	1.54	
500	0.05	3.84	0.24
1 000	0.10	7.68	0.48
2 084	0.21	16.00	1.00
20 000	2.0	153.68	9.60

[1] Ounces per 1000 cubic feet or milligrams per litre

Among the fumigants commonly employed, EDB is one of the more toxic to insects (see Chapter 14, Table 16). Loschiavo (1960) found that female confused flour beetles, Tribolium confusum, were more susceptible than males to very low doses of EDB and that the fecundity and fertility of survivors were reduced. Confused flour beetle adults treated with sublethal doses of EDB laid sterile eggs, in contrast to those fumigated with methyl bromide, which laid fertile eggs (Kazmaier and Fuller, 1959). Insects affected by EDB may remain moribund many days before dying (Bond and Monro, 1961). A low level of resistance to EDB has been found in a population of Tribolium castaneum exposed to repeated treatments over a number of years (Bond, 1973). Ellis and Morrison (1967) described a simple technique for conducting small chamber tests with ethylene dibromide in order to assess the susceptibility of insects under local conditions.

EFFECT ON PLANT LIFE

Seeds

When EDB was used for insecticidal treatments, it appeared to have no effect on the germination of wheat, barley, maize, vetch, peas and beans (Amen et al, 1946). Seeds of high oil content, such as soybean, flax, sesame and groundnut, however, need prompt postfumigation aeration in order that the residual fumigant may not affect germination (Plaut,1957). Sorghum seed is low in oil content as compared with

sunflower seed, but both require the same precautions (Lachover et al, 1958). Ethylene dibromide as a constituent of a fumigant mixture caused significant reduction in germination of maize, sorghum, barley, oats, wheat and rice seeds after 12 months' storage, especially under combined conditions of high moisture content and high temperature, e.g. above 27°C King et al, 1960). C.H. Richardson (1951) also found that EDB was detrimental to the germination of maize.

It is clear that the use of EDD for seed fumigation should be undertaken with caution, preferably after preliminary trials under local conditions.

Growing Plants and Nursery Stock

There is little information on the susceptibility of plants to the vapours of EDB. It has been stated that it is strongly toxic to growing plants but less injurious to dormant ones (Negherbon,1959; Pritchard, 1949). Monro (1955) found that ethylene dibromide in concentrations toxic to the European pine shoot moth, Rhyacionia buoliana (Schiff.), in dormant pine nursery stock caused considerable injury and retardation of subsequent growth. The species of pine tested were red, Scotch, mugho and white, and of these the latter was extremely susceptible. However, EDB has been found effective for dipping, or for injecting soil balls around the roots of nursery stock to prevent the spread of the

Japanese beetle (Fleming et al,1958; Richardson and Balock, 1959) and of the European chafer (Tashiro,1962). Wolfenbarger (1957) reported that dips or surface applications of EDB emulsions did not injure a wide range of nursery and glasshouse plants.

EFFECT ON PLANT PRODUCTS

Fresh Fruit

The use of EDB for the fumigation of fruit came into prominence as a result of the work of Balock (1951) and Balock and Lindgren (1951) on the control of the oriental fruit fly in Hawaii. Generally speaking, fruit appears to be more tolerant to EDB than to methyl bromide at insecticidal concentrations.

An incipient off-flavour is noticed in fruit immediately following fumigation with EDB but it disappears as soon as the gas diffuses from the fruit (Claypool and Vines, 1956).

In the fumigation of fruit, particular attention must be paid to the relationship between dosage and load in the fumigation chamber. EDB is rapidly sorbed and initial residues have been found to be proportional to concentration and exposure time (Chalutz et al, 1971). Packing materials can also have considerable influence on sorption of fumigant and on postfumigation effects. Swaine et al (1976), after fumigating mangoes in cardboard cartons, concluded that the residual fumigant in the carton contributed significantly to the effectiveness of the treatment.

Peel injury, which sometimes occurs in citrus fruit, is related to persistence of residual unchanged fumigant in the fruit. The incidence of peel injury is found to be highest in fruit stored at low temperatures or wrapped in polyethylene bags (Chalutz et al, 1971). Some reduction in peel injury may be obtained by application of the fungicide thiobendazol (Chalutz et al, 1973).

In a study of the tolerance of avocados to EDB for control of Mediterranean fruit fly, Wolfenbarger (1962) found that treated fruit ripened more rapidly than unfumigated fruit. Akamine et al (1954) discussed the factors influencing tolerance or injury in bananas fumigated with EDB to control fruit flies. Farooqi and Hall (1972) concluded that some injury could occur on Australian cavendish bananas when the dose required to kill the Queensland fruit fly (15 g/m for 2 hours at 21.1°C) was used.

Tests on apples have shown that EDB will effectively control apple maggot (Sanford, 1962 a, b) and eggs of European red mite (Bond et al, 1973).

Details of treatments with EDB for fruit are given in schedule J.

Vegetables

Several varieties of vegetables are tolerant to EDB in treatments against fruit flies. Tomatoes may be delayed in ripening (Pratt et al, 1953).

Details of some treatments are given in Schedule K.

Cereals and Milled Foods

Used alone, EDB has found only limited application for cereals and milled food products because it does not penetrate well into large masses or stacks of these materials. In India, EDB has been injected directly into grain stored in bags (Muthu and Pingale, 1955). Flour fumigated with EDB had normal baking properties and bread made from it had a normal taste and odour (Plant and Zelchuch, 1953).

Because of the persistence of EDB in cereal grains, its use has been discouraged for cereal fumigations in some countries (FAD/WHO, 1980).

EFFECT ON PAINTS AND METALS

EDB in vapour or liquid form attacks many paints and some metals (particularly aluminium). This characteristic is important when the material is used in fumigation chambers, as special finishes may have to be used and precautions taken to prevent damage and corrosion. It has been found that catalyst-type paints are not affected during fumigation by the vapours of EDB, whereas standard enamels may soften and wrinkle (Grierson and Hayward, 1959). Gray (1959) described an inhibitor which renders a grain fumigant containing EDB noncorrosive to mill machinery.

RESIDUES IN FOODSTUFFS

Ethylene dibromide, in contrast to methyl bromide, does not normally react to any significant degree with the constituents of foodstuffs, but there is the possibility of the formation of small amounts of inorganic bromide. Other reactions may occur, such as the breakdown of EDB to form ethylene glycol, which may react with the methionine in the wheat protein (Bridges, 1956; Olomucki and Bondi, 1955).

When considering the question of inorganic bromide residues, it must be borne in mind that naturally occurring bromides are found in many foodstuffs (Heywood, 1966) and, therefore, analysis based on inorganic bromide alone may not give a true indication of fumigant residue. Because of the widely differing toxicological effects, it is necessary to determine residues of unchanged fumigant and of bromide ion separately.

The main problem with EDB is that, because of its comparatively low volatility, it is physically sorbed by fumigated materials; considerable aeration and a long interval are required before the vapours are completely dissipated.

Fruits with thick skins are likely to retain small amounts of the fumigant almost indefinitely (Sinclair et al, 1962). Studies by Hargreaves et al, (1978) showed that EDB residues up to 4 mg/kg could occur in fruit and vegetables (e.g. capsicum, mango, papaya, passion fruit, pumpkin and zucchini) after fumigation and they suggested a withholding period of at least five days to allow for Resorption. The levels of residual EDB in apples bested with 12 mg/l of the fumigant for four hours at 13°C declined rapidly in the first two days after treatment but required nearly four weeks at 13°C to desorb to 0.1 mg/kg (Dumas and Bond, 1975). In studies on grapefruit treated to eliminate possible infestation by larvae of the Caribbean fruit fly, King et al (1980) showed that residues were higher in fruit held at lower temperatures but, after three to six days of storage, residues were less than 1 mg/kg in fruit held at 13 or 21°C.

In cereals, the uptake of EDB increases significantly with an increase of moisture content from 9 to 18.5 percent (Berck, 1965b). Uptake is greater in seeds with high fat content and grinding or milling increases sorption. Amuh (1975), using C labelled EDB, found that six weeks were required to remove sorbed EDB from fumigated maize but about 40 percent remained in a chemically bound state for 14 weeks after treatment. On milling of aerated wheat, Sidhu et al, (1975) showed that 18–38 percent of residual EDB was lost but significant residue remained, particularly in bran and shorts. Sensitive analytical methods now available have shown that a minute part of unchanged EDB can be detected in baked goods made from treated wheat. Flour and biscuit samples from commercial channels have been found to contain up to 4 mg/kg residual EDB in flour and 0.26 mg/kg in biscuits (Rains and Holder, 1981).

The problem of residual EDB is likely to be greatest in animal foodstuffs or in foods that are intended for consumption without cooking. Although some surveys of cargoes of imported grain have shown only low levels of residual EDB, at or below 1 mg/kg

(FAD/WHO, 1980), the possibility of significant residues remaining in foodstuffs that have not been adequately aired is viewed with some concern. Jagielski et al (1978) indicated that grain treated in a well constructed farm bin or in a tightly sealed bog may retain residual fumigant at a high level for a considerable period of time.

It is clear that great care must be exercised to ensure that residual vapours of ethylene dibromide are fully dissipated from fumigated foodstuffs before they are consumed. This is particularly important in countries where the material may be treated at temperatures lower than 25°C.

An annotated list of references to residues of EDB found in 8 range of foodstuffs is given in Schedules J and K.

Evaluation of Residues

In the past, residue tolerance recommendations for EDB have been based on bromide ion present in the food material. However, as there is no way of determining the source of the bromide (naturally occurring bromides are present in some foods), the FAO Panel of Experts on Pesticide Residues in Food (FAD/WHO, 1980) indicated that it is unrealistic to regulate residues of EDB or other bromide fumigants on the basis of bromide ion.

Because of the adverse effects of EDB, as demonstrated in various tests on animals and with the availability of more sensitive analytical methods, the FAO panel recommend that the guideline level of EDB for cooked products should be reduced to a figure at or about the new low limit for determination (0.01 mg/kg). For cereal products intended for consumption without cooking, they recommend that the grain be selected from lots not treated with EDB. The guidelines for fruit and vegetables were set in line with residue levels known to occur at the end of suitable withholding periods after treatment e.g. 0.5 mg/kg for citrus and passion fruit, 0.1 mg/kg for other fruit and vegetables.

METHODS OF ANALYSIS

Determination of Vapours

Concentrations of EDB in air can be determined with considerable precision by gas chromatography using thermal conductivity or flame ionization detectors (Berck, 1965a; Dumas and Bond, 1975; Swaine et al, 1976). If necessary, samples can be taken in suitable containers for transport to the laboratory; however, due allowance for sorption on the walls of the sampling container may be necessary. Jonsson and Berg (1980) described a method for rapid and simultaneous determination of trace concentrations of EDB and EDG in ambient air, using a porous polymer for collection of the sample and gas chromatography for analysis. Dumas and Bond (1982) outlined a method for direct micro determination of EDB in air.

The infra-red gas analyser (described in Chapter 3) is described as being capable of measuring concentrations of EDB from 0.1 to > 8 100 ppm and the portable gas chromatograph is sensitive down to 0.01 ppm or less. Chemical methods based on the Volhard titration have been successfully used for determining concentrations of EDB (Sinclair and Crandall, 1952; Kennett, 1954). A colorimetric method for analysis of levels as low as 1 ppm in air and 0.5 ppm residue in grain has been described by Rangaswamy et al (1976).

The thermal conductivity analyser described in Chapter 4 is not recommended for use with EDB because high sorption from the materials in the guard tubes results in an extremely slow response.

<u>Determination of Residues</u>

Low levels of residual EDB in commodities can be determined by gas chromatography using electron capture detectors. A cold extraction procedure developed by Heuser and Scudamore (1969b) was established, by a Panel on Fumigant Residues in Grain (1974), to be suitable for residue determination in maize and wheat. For residues in fruit, steam distillation procedures followed by gas chromatography have been found suitable for determinations down to levels of 0.01 mg/kg (Bielorai and Alumot, 1966; Dumas and Bond, 1975). King et al (1950) described an electron capture gas chromatographic method for determination of EDB residues in grapefruit down to 0.00038 mg/kg and Hargreaves et al (1974) gave a method for estimation of EDB in vegetables.

EDB residues in whole and milled wheat have been determined by benzene extraction followed by azeotropic disillation of the extract with water and iodometric estimation as bromide ion after breakdown by alcoholic potash (Sidhu et al, 1975).

Inorganic bromide can be determined by the method of Kennett and Huelin (1957). For determinations intended to differentiate between organic bromide and bromide ion, a non-aqueous solvent extraction procedure should be used rather than a heating process that can break down EDB.

APPLICATION

This fumigant is often a component of liquid-type fumigant mixtures, as described in Chapters 7 and 10. Owing to its sorption by grain, its use alone should be undertaken with caution.

When the fumigant is used in a conventional fumigation chamber, it is necessary to volatilize it by heating. This is done by pouring it onto an enamel or stainless steel pan heated by an electric hotplate, or other convenient means without a flame, or by glowing wires exposed to the gas (Richardson and Balock, 1959). This gas is more than six times as heavy as air and vigorous circulation by fans or blowers is needed to

provide even distribution. Condensation of the vapour can occur if air movement is insufficient for thorough mixing of the fumigant with air.

Muthu (1964) devised a method of applying EDB in small amounts for treatment of individual Lags or of individual small storages, such as split bamboo bins, used in Indian homes or farms. The required amount of EDB is impregnated in small cardboard discs, which are then sealed in aluminium foil envelopes.

In Ghana (Hall, 1963), an experiment was carried out in which maize was stored in jute bags with 500-gauge polyethylene liners, 149 of ethylene dibromide being applied to each bag on a pad of cotton wool before the liner was tied and the bag sewn. This treatment gave 100 percent control and will, it is claimed, give protection for as long as the polyethylene remains intact.

ETHYLENE OXIDE

As an insecticide, the principal use of ethylene oxide (ETO) has been for fumigation of bulk grain in recirculating systems and in the vacuum fumigation of packaged foods and tobacco. It has also proved to be effective both under vacuum and at atmospheric pressure for destroying several species of snails entering the United States in military cargoes from the Mediterranean area (Richardson and Roth, 1963), see Schedule T. In recent years, ETO has been used extensively for the cold sterilization of medical supplies and instruments, for preventing spoilage in foodstuffs and spices and also for controlling diseases in honeycombs and equipment from honeybee colonies. For information on the use of ETO for sterilization, reference may be made to the following: Rauscher et al (1957); Mayr and Kaemmerer (1959); Bruch (1961); Mayr (1961); Phillips (1961); Stierli et al (1962); Moeller et al (1972); Cantwell (1975).

FLAMMABILITY

Ethylene oxide is flammable within wide limits. It is therefore necessary in many commercial applications to mix it with a non-flammable carrier. It is obtainable mixed with carbon dioxide in the proportion of one part ETO to nine parts CO2 by weight or lt or 12 percent ETO with non-flammable halogenated hydrocarbon refrigerant gases. The flammability limit of ethylene oxide - methyl bromide - air mixtures is given by Hashigochi et al (1967).

PROPERTIES OF ETHYLENE OXIDE
ALTERNATIVE NAMES: 1, 2-EPCXYETHANE, OXLRANE
ABBREVIATION USED IN THIS MANUAL : ETO

ODOUR	Irritating, mustard-like. May be hard to detect in low concentrations
CHEMICAL FORMULA	$(CH_2)_2O$
BOILING POINT	10.7°C
FREEZING POINT	-111.3°C
MOLECULAR WEIGHT	44.05
SPECIFIC GRAVITY	
GAS (AIR = 1)	1.521
LIQUID (WATER AT 4°C = 1)	0.887 at 7°C
LATENT HEAT OF VAPORIZATION	139 cal/g
FLAMMABILITY LIMITS IN AIR	3 to 80% by volume
SOLUBILITY IN WATER	Infinite at 0°C
PERTINENT CHEMICAL PROPERTIES	Highly reactive and flammable; relatively noncorrosive
METHOD OF EVOLUTION AS FUMIGANT	By discharge by natural pressure from gas cylinders. Owing to high flammability, usually mixed 1 : 9 with carbon dioxide.
COMMERCIAL PURITY	99.5%

Natural vapour pressure at different temperatures

0°C (32°F) 493.1 mm Hg
10°C (50°F) 738.0 mm Hg
20°C (68°F) 1 095.0 mm Hg

Weights and volumes of liquid

1 lb (avdp) at 7°C has volume 511.4 ml
1 U.S. gal weighs 7.4 lb (3.354 kg)
1 Imp gal weighs 8.87 lb (4.023 kg)
1 kg has volume 1 127.39 ml
1 litre weighs 0.887 kg

Dosages and concentrations of gas in air (25°C AND 760 MM PRESSURE)

BY VOLUME		WEIGHT PER VOLUME	
PARTS PER MILLION	PERCENT	[1]G/M³	LB/L 000 FT³
50	0.005	0.09	
100	0.01	0.18	
200	0.02	0.36	
500	0.05	0.90	
555	0.055	1.00	
1 000	0.10	1.80	0.11
8 885	0.89	16.00	1.00
20 000	2.0	36.01	2.25

[1] Ounces per 1000 cubic feet or milligrams per litre

TOXICITY

Despite a general impression to the contrary, ETO must be regarded as poisonous to humans by inhalation, although it is not as lethal in comparatively low concentrations as some other fumigants. The acute toxic effects of ETO in humans and animals include acute respiratory and eye irritation, skin sensitization, vomiting and diarrhoea. Skin injury may result from excessive freezing following spillage of the chemical. Continuous exposure to even low concentrations may result in a numbing of the sense of smell.

Known chronic effects consist of respiratory irritations and secondary respiratory infection, anaemia and altered behaviour. Although limited tests on mice have not revealed carcinogenic effects, the alkylating and mutagenic properties of ETO are sufficient to cause concern (Glaser, 1979). Health authorities recommend that ETO be considered as potentially carcinogenic to humans and that occupational exposure to it should be minimized by eliminating all unnecessary and improper uses. The threshold limit for continuous daily breathing is presently listed by the American Conference of Governmental Industrial Hygienists (ACGIH, 1981) for change from 10 to 5 ppm.

Of the commonly used fumigants, ethylene oxide is about intermediate in toxicity to insects (see Chapter 14, Table 16).

EFFECT ON PLANT LIFE

Ethylene oxide reacts strongly with living plant material, causing either death or extreme injury. It is not usually recommended for use on seeds (Joubert and Du Toit, 1965), nursery stock or any growing plants.

A report by Steinkraus et al (1959) shows that some species of air-dried seeds containing 5 to 10 percent moisture may be tolerant to bactericidal and fungicidal treatments with ethylene oxide.

The tolerant seeds did not lose viability after exposure to pure atmospheres of ethylene oxide for periods up to one hour at 27°C. On the basis of the concentration x time (c x t) products, the treatments for 60 minutes would be assumed to be highly insecticidal. The tolerant seeds were onion, aster, mung bean, spinach, lucerne, pea, dandelion, Sudan grass and radish.

Seeds that suffered serious loss of germination were garden bean, pea bean, red kidney bean, carnation, barley, oats, wheat, maize (including sweet corn), mignonette, anchusa and nasturtium. The germination of lucerne seed was seriously impaired by quick dipping or soaking in water before fumigation.

Because this gas is both insecticidal and toxic to some micro-organisms, its use may be especially valuable for the production of disease-free and insect free seed of the tolerant species. A method for the elimination of microflora from barley kernels with ethylene oxide has been described by Bushnell (1973).

EFFECT ON PLANT PRODUCTS

Fresh Fruit and Vegetables

Although some fresh fruit (blackberries and blueberries) have shown tolerance to ETO in treatments against insects, severe injury occurs to bananas (Osburn and Lipp, 1935) and other fruit and vegetables (Lepigre, 1947). It would be unwise to attempt any treatment of fruit and vegetables with this gas without preliminary experiments.

Cereals and Milled Foods

At atmospheric pressure, ethylene oxide does not penetrate well into bagged and packaged cereals and milled products (Lepigre, 1947). It is used for this type of material mainly in vacuum fumigation. Its use as a fumigant for treating bulk grain by recirculation in silos is discussed in Chapter 10.

Dried Fruit

Ethylene oxide is used in the dried fruit industry to stop microbial spoilage in prunes and, presumably, these treatments are also insecticidal.

EFFECT ON FOODSTUFFS

Ethylene oxide has been used for over 40 years for both insecticidal treatments and for the sterilization of foodstuffs. A number of investigations have shown that it will react with food constituents and disturb the nutritional value of food. Modification of colour,

taste, odour and texture of foodstuffs may occur (Kroeller, 1966) but many materials can be fumigated without appreciable change in these properties. Nearly all spices can be fumigated with little or no change; however, slight alteration of colour and taste has been observed in spices such as mustard seed and turmeric (Mayr and Suhr, 1973). The chemical composition of flour has been reported by Koyanagi et al (1963) to show some changes but no marked deterioration in baking quality was found.

Vitamins of the B complex and some of the amino acids may be destroyed when exposed to ETO; however, drier conditions may reduce this effect. Charles et al (1965) found that, in a dry sterilization procedure where the efficiency of the treatment was satisfactory, the effect on vitamin B content was only slight in comparison to steam sterilization.

Although Hawk and Mickelsen (1955) found that the growth rates of rats was restricted when the animals were fed a diet treated with a high level of ETO for 18 hours, feeding trials carried out on rats and mice over several generations (Charles et al, 1965) showed that animals fed a diet treated for eight hours, with subsequent complete aeration, had the same growth rates and litter sizes as those on untreated diets. Sterilization procedures for various diets for laboratory animals, including fish, have also been developed (Ready et al, 1968; Trust and Wood, 1973).

RESIDUES IN FOODSTUFFS

Chemical residues in commodities treated with ETO may occur as follows: unchanged ETO, which may persist for some time after the treatment; compounds of low molecular weight, such as ethylene chlorohydrin, ethylene bromohydrin and ethylene glycol, produced by interaction of LTO with inorganic constituents of the commodity; alkylated and hyrdroxyethylated derivatives of food constituents such as sugars, amino acids, vitamins and proteins.

When treated commodities were kept at 25°C, either under air tight storage conditions or in the open air, Scudamore and Heuser (1971) found that residual ethylene oxide usually fell below 1 mg/ky within 14 days; however, flour treated at high levels for sterilization and kept under air tight conditions retained 50–100 my/kg in this time and traces were found after 90 days. At lower temperatures ETO disappeared more slowly. Pfeilsticker and Rasmussen (1974) showed that the fumigant is preferentially bound in the aleuron cells and the embryo of wheat kernels.

The detection of the reaction product ethylene chlorohydrin was reported by Wesley et al (1965) and ethylene bromohydrin was found in flour and wheat previously treated with methyl bromide before ETO (Heuser and Scudamore, 1969a). Levels of ethylene chlorohydrin produced by exposure to ETO ranged from zero in groundouts and cocoa beans treated at insecticidal levels to thousands of parts per million in sterilized curry powder and turmeric. Stijve et al (1976) found that the amount of ethylene chlorohydrin formed in fumigated flour was roughly proportional to the inorganic chloride content, while in other commodities, notably mushrooms, it was much less.

The persistence of ethylene chlorohydrin varied considerably with the type of food; dehydrated mushrooms lost 7080 percent within 4 months whereas no decrease was observed after the same period in black pepper and whole turmeric. In the preparation of baked and steamed products from flour containing ethylene chlorohydrin and ethylene bromobydrin, Scudamore and Heuser (1971) found that 20 to 100 percent of the residue was lost, depending on the alkalinity of the material.

Using radioactive ETO, Pfeilsticker and Rasmussen (1974) found that 85 percent of the bound fumigant in wheat was converted to water-soluble compounds. The radioactivity was distributed among various substarices, including proteins, organic acids, saccharides, lipids and starch. A method for determination of ethylene chlorohydrins in foods was outlined by Ragelis et al (1966) and one for the identification of 2 - chloroethyl esters of fatty acids in spices and foods was given by Heike and Griffitt (1979).

Scudamore and Heuser (1971) concluded that residual amounts of ETO and glycols in foodstuffs after fumigation are unlikely to constitute a hazard and that the ethylene chlorohydrin formed in otherwise significant amounts may partly disappear during storage and cooking.

METHODS OF ANALYSIS

Determination of Vapours

For field use the sachet method of Heseltine and Royce (1960, see Chapter 4) may be used to indicate the attainment within limits of 10 percent of required concentration x time (c x t) products, with the aid of a simple titration conducted on the spot. There are also available on the market indicator tapes for sterilization with ETO but apparently there is no record of them having been used for insecticidal fumigations.

Richardson and Roth (1963) found that the thermal conductivity analyser could be used in practical fumigations for the ethylene oxide-carbon dioxide mixture. They describe their procedure in detail. With heavy loads of sorptive material, which remove ETO from the atmosphere but do not take up CO2, the method was not sufficiently accurate for a close control of ETO concentrations. Used in conjunction with the sachets of Heseltine and Royce (1960), however, these authors found that the thermal conductivity analyser could be used effectively in certain field applications. Detector tubes, described in Chapter 4, give good readings for ETO in insecticidal concentrations. The presence of CO2 made no difference (Dumas and Monro, 1966).

Methods for monitoring exposure to ethylene oxide in the occupational environment have been described by Qazi and Ketcham (1977) and Romano and Renner (1979).

Determination of Residues

The standard method for determination of residual ETO vapours in foodstuffs is that of Lubatti (1944). This is based on bubbling the atmosphere under test through dilute sulphuric acid solution containing a high concentration of magnesium bromide. Ethylene bromohydrin is formed and sulphuric acid is consumed in the process. The unused acid is titrated with standard sodium hydroxide solution to indicate the amount of ETO consumed by the acid. This method has been further developed by Hollingsworth and Waling (1955) and also by Benedict (1957), who described a simplified procedure for determining the residual ETO in fumigated copra.

The employment of the techniques of yes chromatography has been reported by Kalinenko and Naimushin (1961), Berck (1965a), Staszewski, et al (1965), Gafarova, et al (1966) and Dumas (1976). A comparison of analytical methods for residual ethylene oxide analysis was given by Romano and Renner (1979).

APPLICATION

For use as an insecticide, this fumigant is usually marketed in steel cylinders containing 30 or 60 lb (14 or 28 kg) of the 1 : 9 mixture with CO_2. For some applications in specially designed equipment, under expert supervision, there is also available a mixture of 90 percent ETO and 10 percent CO_2. At normal temperatures, the 1 : 9 mixture in the cylinder exerts a pressure of about 80 atmospheres. In vacuum fumigation, the cylinder containing the mixture is sometimes first discharged into a large storage tank or "accumulator" where it is warmed up before being introduced into the evacuated Fumigation chamber. The object of this step is to provide a homogeneous mixture in the fumigation system from the beginning of the treatment.

For use as a sterilizing agent, ETO is available as an aerosol mixed with propellants of the Freon type. Ethylene oxide constitutes 11 percent of the mixture and may be discharged from the container without the risk of fire or explosion.

For insect control in foodstuffs fumigated under vacuum, a usual application rate is 100 g/m for three hours at temperatures between 20 and 25°C and for sterilizing foodstuffs, 500 g/m for six hours at similar temperatures.

PRECAUTIONS

Fire and Explosion Hazards

Unless special precautions are taken, there is danger of fire or explosion when ETO is being used. An explosion of the 1 : 9 mixture (ETO : CO_2) may be caused by a static spark generated while the gas mixture is passing through a metal tube on its way from the cylinder to the chamber. Therefore, precautions must be taken against the building up of static electricity, by earthing all equipment.

Protection of Personnel

Protection against the inhalation of ETO is afforded by a respirator fitted with a standard "organic vapours" canister, as long as the concentration of the fumigant does not exceed 2 percent by volume. It must be remembered, however, that the canister does not protect against inhalation of CO2 which, at high concentrations in air, may rapidly produce giddiness and suffocation. This is due not only to the direct action of CO2 on the respiratory centres, but also to the reduction of the oxygen content of air by the presence of excess CO2. For instance a dosage recommended for atmospheric fumigation chambers is 400 g/m^3 (25 lb/1000 ft^3) for 12 to 24 hours. The atmosphere in an empty chamber would thus contain 2.2 percent ETO and 19.8 percent CO2. Self-contained respirators or continuous flow air-line respirators that supply breathing air for prolonged periods in hazardous atmospheres may be useful in such situations.

In the normal use of ETO in confined spaces, such as grain silos and fumigation chambers, the chances of exposure to high concentrations of ETO sad CO? are slight. Because the respirator cannot be relied upon to give protection against the mixture, attempts should not be made to enter places containing full fumigation concentrations, except in cases of extreme emergency. Under such circumstances, an air-line hose mask or self-contained breathing apparatus should be used.

ETHYLENE DICHLORIDE

Ethylene dichloride (EDC) is not as toxic to insects as other commonly used fumigants, but it is useful in the fumigation of grain and seeds. Because both the vapours and the liquid are flammable, EDC is mixed with some non-flammable material, usually carbon tetrachloride (CT) in the proportion of three parts EDC to one part CT by volume. The mixture, applied according to recommendations, has no adverse effect on the germination of seeds or the milling qualities of grain (Cotton, 1963). Care must be taken to avoid excessive exposure (Caswell and Clifford, 1958). Although some plants appear to be tolerant to EDC, severe injury has been recorded with certain species. Some fruits are also tolerant (Claypool and Vines, 1956). This fumigant, therefore, should not be used alone or in a mixture for fumigating nursery stock, living plants or vegetables without careful preliminary experiments on the particular species or varieties concerned.

EDC has been used in emulsion with water against the peach tree borer when soil temperatures were too low for effective use of paradichlorobenzene (Snapp, 1939). Some injury has been reported to peach trees.

Because EDC is soluble in fats and oils, it is not recommended for use on cereals or foods with high oil content.

TOXICITY

Ethylene dichloride has the property of causing injury to the human liver and kidney from either excessive single or repeated exposures. Acutely, it is somewhat more toxic than carbon tetrachloride and under these conditions is also a central nervous system depressant and lung irritant. Recent research has shown that high dosage levels of EDC can cause tumours in rats and mice (National Cancer Institute, 1978) and this observation has led some countries to regulate the use of EDC so that adequate precautions against accidental exposure may be taken.

In practice, most people will not tolerate or will be nauseated by sublethal concentrations (see the section on precautions below).

Information on the toxicity of EDC to insects is given in Chapter 14 (Table 16).

RESIDUES IN FOODSTUFFS

During fumigation of cereal grains with ethylene dichloride or its mixture with other halogenated hydrocarbons, relatively heavy and continuous sorption of the fumigant takes place (Winteringham, 1944). The amount sorbed is higher at lower temperatures. The adsorbed fumigant airs off slowly from whole grains over a period of months. During handling, cleaning or milling processes, the amount of adsorbed fumigant is progressively reduced (Lynn and Vorhes, 1957). After milling, a greater proportion of ethylene dichloride is found in the bran than in the whole grain before milling (Conroy et al, 1957).

PROPERTIES OF ETHYLENE DICHLORIDE
ALTERNATIVE NAME: 1, 2 DLCHLOROETHANE
ABBREVIATION USED IN THIS MANUAL : EDC

ODOUR	Like chloroform
CHEMICAL FORMULA	$CH_2Cl.CH_2Cl$
BOILING POINT	83.5°C
FREEZING POINT	−35.3°C
MOLECULAR WEIGHT	98.97
SPECIFIC GRAVITY GAS (AIR = L)	3.42
LIQUID (WATER AT 4°C = 1)	1.257 at 20°C
LATENT HEAT OF VAPORIZATION	85.3 cal/g
FLAMMABILITY LIMITS IN AIR	6.2 to 15.9% by volume
SOLUBILITY IN WATER	0.869 g/100 ml at 20°C
PERTINENT CHEMICAL PROPERTIES	Flash point 12 to 15°C. Stable and noncorrosive
METHOD OF EVOLUTION AS FUMIGANT	By evaporation of liquid. Always used in mixture with non-flammable fumigant or carrier, such as carbon tetrachloride

Natural vapour pressure at different temperatures

0°C (32°F) 23 mm Hg
10°C (50°F) 40 mm Hg
20°C (68°F) 65 mm Hg
25°C (77°F) 81.0 mm Hg
30°C (86°F) 103.0 mm Hg
40°C (104°F) 160.0 mm Hg

Weights and volumes of liquid

1 lb (avdp) at 20°C has volume 360.8 ml
1 U.S. gal weighs 10.47 lb (4.753 kg)
1 Imp gal weighs 12.57 lb (5.702 kg)
1 kg has volume 795.5 ml
1 litre weighs 1.257 kg

Dosages and concentrations of gas in air (25°C AND 760 MM PRESSURE)

BY VOLUME		WEIGHT PER VOLUME	
PARTS PER MILLION	PERCENT	[1]G/M³	LB/L 000 FT³
50	0.005	0.20	
200	0.02	0.81	
247	0.025	1.00	
500	0.05	2.02	0.13
1 000	0.10	4.05	0.25
3 953	0.395	16.00	1.00
20 000	2.0	80.95	5.06

[1]Ounces per 1000 cubic feet or milligrams per litre

Wheat treated at 1 l/m³ (9 gallons/1 000 bushels) with 3 : 1 ethylene dichloride/carbon tetrachloride mixture, triple the dose recommended by the United States Department of Agriculture, showed a maximum of 140 mg/kg ethylene dichloride three days after application of the fumigant. Loss of fumigant during tempering and cleaning processes was up to 70 percent and the maximum residue found in the flour made from this batch was 5 mg/kg. Other investigations have shown similar results, with a gradual reduction in the residue level over a number of weeks; the level of EDC in bread made from white flour of treated wheat was generally below 0.05 mg/kg (FAD/WHO, 1980). Similar desorption has been shown to take place when flour is fumigated with EDC and baking tests carried out after seven days of airing, have shown no detectable reduction in baking quality and no taint of the fumigant in the finished bread.

When added to grain fed to cows, at levels up to 1 000 mg/kg an average of less than 0.25 mg/kg ethylene dichloride was found in the milk. There appears to be no direct correlation between amounts of ethylene dichloride added to the grain and that found in the milk (Sykes and Klein, 1957). In a two-year test on laying hens with EDC at 250 and 500 mg/kg in the diet Alumot et al, (1976) reported a decrease in egg weight from month four and egg production was affected at 500 mg/kg.

The guideline tolerances for residues of EDC recommended by FAO (FAD/WHO, 1980) are 50 mg/kg for cereal grains, 10 mg/kg for cereal products intended for cooking and 0.1 mg/kg for bread and other cooked cereal products.

METHODS OF ANALYSIS

Residual EDC in stored products can be determined by gas chromatography, following cold extraction with acetone-water solvent (Heuser and Scudamore, 1969b) or after

continuous solvent co-distillation from a suspension using toluene and boiling water (Bielorai and Alumot, 1966). Page and Kennedy (1975) used vacuum distillation and gas chromatography for determination of residues in spice oleoresins. A method for analysing residues in biological samples was given by Zuccato et al, (1980).

Winteringham (1942, 1944) described a method for recovering EDC from foodstuffs with analysis by the Volhard titration.

APPLICATION

The EDC/CT mixture is a liquid at ordinary temperatures, and its application for grain fumigation is described in Chapter 10.

If it is used in a fumigation chamber, as for instance with bagged seed, the liquid may be poured into a shallow pan or directly onto the bags. Vigorous circulation with a fan or blower is needed during the first hour of treatment for complete volatilization of the liquid and even distribution of the gas, which is much heavier than air.

PRECAUTIONS

Ethylene dichloride has a strong, sickly, chloroform-like odour, detectable at about 50 ppm in air, which gives ample warning of unsafe concentrations (Rowe, 1957). The dosage of EDC/CT mixture usually recommended for space fumigation is between 224 and 288 g/m (14 to 18 lb/l 000 ft^3). This is above 2 percent by volume in air of the mixture of the two gases. Therefore, a standard industrial-type respirator will not protect against a full fumigation concentration. However, because the mixture is applied as a liquid, a respirator is useful before the full concentration is reached. One should be worn when the fumigant is being poured during application in a chamber to the surface of bulk grain or to the grain stream. A respirator with a fresh canister may also be worn when the space is entered after fumigation following a period of preliminary aeration. The odour of the two ingredients of the mixture should indicate whether or not protection is being given by the canister.

CARBON DISULPHIDE

Carbon disulphide (CS_2) was one of the first fumigants employed on a large scale. Its use in France, in 1869, against the grape phylloxera is a landmark in the history of applied entomology. It was injected into the soil to control the insects infesting the roots of the grapevine. For many years afterwards, CS_2 was widely used as a soil or space fumigant. Its tendency to burn or explode presents a hazard, and many explosions have been recorded during its use as a fumigant (Hinds, 1911; Fleming and Baker, 1935).

Carbon disulphide penetrates well and is still the only fumigant used in certain parts of the world. It is of practical value in tropical countries where the high temperatures favour volatilization.

Carbon disulphide is commonly formulated in mixtures with non-flammable ingredients for fumigating grain.

TOXICITY

Judged on the basis of lethal dosages, CS_2 ranks rather low among the insect fumigants because relatively large dosages by weight are required.

Carbon disulphide is toxic to humans. Because it is used in certain manufacturing processes, it is an important industrial poison. High concentrations of the vapour produce a narcotic effect and, if exposure is continued, unconsciousness and death may ensue from paralysis of the respiratory cent ret Repeated exposure to low concentrations for periods of a few weeks or longer may result in a variety of nervous manifestations, which may make correct diagnosis difficult (Canada, Department of National Health sod Welfare, 1957). Persons exposed to low concentrations may lose their ability to detect the odour of the chemical and thus may continue to work in a toxic atmosphere without being aware of it (Hinds, 1917).

PROPERTIES OF CARBON DISOLPHIDE
ALTERNATIVE NAME : CARBON BISULPHIDE
ABBREVIATION USED IN THIS MANUAL: CS2

ODOUR	Sweetish when pure; impurities, such as hydrogen sulphide, give characteristic unpleasant odours
CHEMICAL FORMULA	CS_2
BOILING POINT	46.3°C
FREEZING POINT	-111 C
MOLECULAR WEIGHT	76.13
SPECIFIC GRAVITY	
GAS (AIR = 1)	2.64
LIQUID (WATER AT 4°C = 1)	1.2628 at 20°C
LATENT HEAT OF VAPORIZATION	84.1 cal/g
FLAMMABILITY LIMITS IN AIR	1.25 to 44% by volume
SOLUBILITY IN WATER	0.22 g/100 ml at 22°C
PERTINENT CHEMICAL PROPERTIES	Flash point about 20°C and ignites spontaneously about 100°C
METHOD OF EVOLUTION AS FUMIGANT	By evaporation of liquid; now used more often in non-flammable mixtures
COMMERCIAL PURITY	99.99%

Natural vapour pressure at different temperatures

0°C (32 F) 127.3 mm Hg
10°C (50°F) 198.1 mm Hg
20°C (68°F) 297.5 mm Hg
25°C (77°F) 351.1 mm Hg
30°C (86°F) 432.7 mm Hg
40°C (104°F) 616.7 mm Hg

Weights and volumes of liquid

1 lb (avdp) at 20°C has volume 359.2 ml
1 U.S. gal weighs 10.53 lb (4.775 kg)
1 Imp gal weighs 12.63 lb (5.728 kg)
1 kg has volume 791.89 ml
1 litre weighs 1.2628 kg

Dosages and concentrations of gas in air (25°C AND 760 MM PRESSURE)

BY VOLUME		WEIGHT PER VOLUME	
PARTS PER MILLION	PERCENT	[1]G/M³	LB/1 000 FT³
20	0.002	0.06	
50	0.005	0.15	
100	0.01	0.31	
200	0.02	0.62	
321	0.032	1.00	
500	0.05	1.56	0.10
1 000	0.10	3.11	0.19
5 138	0.514	16.00	1.00
20 000	2.0	62.28	3.89

[1] Ounces per 1000 cubic feet or milligrams per litre

Absorption of high concentrations may take place through the skin as well as by inhalation. Prolonged contact of the skin with high concentrations of vapour or with the liquid may result in severe burns, blistering or neuritis (Canada, Department of National Health and Welfare, 1957).

A full discussion of the toxicology of CS_2 is given in a joint FAD/WHO report (1965a).

EFFECT ON PLANT LIFE

Hinds (1917) found that CS_2 in insecticidal fumigations did not reduce the viability of dry seeds (normal moisture content for safe storage). The percentage germination of moist seeds was significantly lowered. Kamel and Shahba (1958) found that the germination of cereal grains (wheat, barley, millet and rice) was not affected with normal fumigation concentrations (250 g/m^3 for 24 hours). Fifteen kinds of vegetable seeds were also not affected, the only exception being eggplant seeds. King et al (1960) experimented with CS_2 as an ingredient of fumigant mixtures with carbon tetrachloride and sulphur dioxide. The seeds used were barley, oats, wheat, rice, cotton and two varieties each of maize and grain sorghum. They concluded that the CS_2 in combination tended to reduce germination, especially after prolonged storage. The reduction was greater when sulphur dioxide was included in the formulation.

Growing plants and nursery stock are severely injured or killed when treated with gaseous CS_2. However, CS_2 applied as a dilute emulsion in water to the earth surrounding the roots of evergreen and deciduous nursery stock in the field is effective against some insects, such as the larvae of the Japanese beetle, without causing injury. For details of these treatments and the specific plant reactions to them, the original work of Fleming and Baker (1935) should be consulted.

EFFECT ON PLANT PRODUCTS

Certain fruits (strawberries, raspberries, blackberries, peaches, plums, red currants and gooseberries) in marketable condition were found to be tolerant to fumigation with CS_2 at 100 g/m^3 (6.25 lb/1 000 ft^3) for 2 hours at 27°C. Their flavour and appearance were not affected. Blueberries did not keep well following treatment, and part of the bloom was removed (Osburn and Lipp, 1935). There appears to be no record of the application of CS_2 fumigation to fruit in commercial practice.

Previously, CS_2 WAS used extensively in fumigation chambers for the treatment of plant products, such as dried beans and peas. Although still used to some extent for this purpose, it has been largely replaced by methyl bromide, which is non-flammable and more easily volatilized.

Majumder et al (1961) reported that CS_2 affects the taste of coffee when used to fumigate monsooned (high moisture content) beans and Calderon et al (1970) that it reducer) loaf volume of bread made from fumigated wheat.

RESIDUES IN FOODSTUFFS

Theoretically, from the results of in vitro studies, CS2 may react with peptides and amino acid groups in foodstuffs of vegetable origin (FAO/WHO, 1965a). However, reaction products of CS_2 fumigation in foodstuffs have not, apparently, been demonstrated as residues.

The available information refers to the possibility of CS_2 itself appearing as residue in fumigated material. Studies of the retention of the fumigant in flour, wheat, rolled oats and the ingredients of bread showed that residues following normal aeration will not persist in cooked foods, such as bread and rolled oats (Lynn and Vorhes, 1957; Munsey et al 1957) .

METHODS OF ANALYSIS

Determination of Vapours

For determination of insecticidal concentrations in the field the thermal conductivity analyser may be used after appropriate calibration for CS_2

(Kenaga, 1958). A chemical method that is fairly rapid and convenient has been described by Fleming and Baker (1935). It is based on direct iodometric titration after the vapours are absorbed by alcoholic potassium hydroxide.

For protection of personnel from the poisonous effects of low concentrations and for the measurement of higher levels, glass detector tubes with ranges as low as 5 ppm and up to 3 200 ppm are available. Also infra-red gas analysers can be used for carbon disulphide. Instruments that will detect concentrations from 0.5 ppm to more than 39 000 ppm can be obtained.

Determination of Residues

Dunning (1957) and Keppel and Munsey (1957) described adaptations of Lowen's dithiocarbamate method for the determination of CS_2 in fumigated products. Berck (1965a) included it among the fumigant gases which may be analysed by gas chromatography. Bielorai and Alumot (1966) described an electron-capture yes chromatography method sensitive to parts per thousand million, although with standard mixtures the recovery was 50 percent or less. Whitney (1962) discussed methods of inhibiting CS_2 decomposition during gas chromatography procedures.

APPLICATION

Carbon disulphide is available in metal cans or drums of various sizes and is readily poured from a large container into a smaller one for application .

The boiling point of CS_2 (46°C) is well above normal temperatures, and in space fumigations some means of rapid volatilization must be provider! in order that the needed concentrations may be reached as quickly as possible. For small-scale work, the liquid may be poured onto some absorbent material such as jute cloth (burlap), which is then suspended in the space. The liquid may also be applied as a fine spray from a spray pump, preferably from outside the building.

An apparatus for rapid vaporization of CS_2 for use in atmospheric fumigation chambers is described by Weigel et al (1927). The CS_2 is poured into a shallow pan containing coils of 0.5 inch (1.3 cm) seamless copper tubing through which hot water is circulated. The temperature of the water must be kept well below 96°C because this is the lowest temperature reported for the ignition of CS_2 in contact with copper. The authors recommend that the temperature of the water in the coil should not exceed 84°C.

Grain fumigation with CS_2 is discussed in Chapter 10.

PRECAUTIONS

Flammability

The low ignition temperature of CS_2 makes it a dangerous fire hazard.

Cans or drums containing liquid CS_2 should be stored in cool, shaded, well-ventilated rooms, never under direct sun. In very hot weather, it may be necessary to spray the containers with cold water to prevent excessive rise in temperature. Contact of the vapour with a steam pipe or an electric light bulb may be enough to ignite it. Even the heat generated by a heavy blow could set off an explosion. The spark from static electricity or from an electric motor is a particularly dangerous source of ignition.

Great care must therefore be exercised in handling this material and strict precautions must be adopted during fumigation. If the grain to be fumigated is heating or is likely to do so, pure CS_2 should not be used.

CARBON TETRACHLORIDE

Carbon tetrachloride (CT) may be used alone as a fumigant but because of its low toxicity to insects, high dosages or greatly prolonger) exposure periods are needed. It has, however, been used alone for grain fumigation, usual lie when there is a shortage of more toxic materials.

At recommended insecticidal concentrations, CT does not affect the germination of seeds (King et al, 1960) hut it may be injurious to growing plants, nursery stock, fruit and vegetables*. Majunder et al, (1961) reported that the taste of coffee may be affected from monsooned (high moisture content) beans fumigated with CT.

* Roth (personal communication, 1967) states that CT in high concentrations near the saturation limit in air for exposures of 4 hours and upward at 25 to 30°C was injurious to seeds of the conifers Pinus, Picea, Larix and Thuja but apparently nut of Cupressus.

PROPERTIES OF CARBON TETRACHLORIDE
ALTERNATIVE NAME : TETRACHLOROMETHANE
ABBREVIATION USED IN THIS MANUAL : CT

ODOUR	Characteristic and well-known
CHEMICAL FORMULA	CCl_4
BOILING POINT	76.8°C
FREEZING POINT	-22.8°C
MOLECULAR WEIGHT	153.84
SPECIFIC GRAVITY	
GAS (AIR = 1)	5.32
LIQUID (WATER AT 4°C = 1)	1.595 at 20°C
LATENT HEAT OF VAPORIZATION	46.4 cal/g
FLAMMABILITY LIMITS IN AIR	Non-flammable
SOLUBILITY IN WATER	0.08 g/100 ml at 20°C
PERTINENT CHEMICAL PROPERTIES	Non-flammable and nonexplosive, relatively inert
METHOD OF EVOLUTION AS FUMIGANT	By evaporation of liquid. Used more often in a mixture to reduce flammability of more toxic fumigants or to act as a carrier for better distribution

<u>Natural vapour pressure at different temperatures</u>

0°C (32°F) 32.9 mm Hg
10°C (50°F) 56.0 mm Hg
20°C (68°F) 91.0 mm Hg
25°C (77°F) 114.5 mm Hg
30°C (86°F) 143.0 mm Hg
40°C (104°F) 215.8 mm Hg

<u>Weights and volumes of liquid</u>

1 lb (avdp) at 20°C has volume 284.4 ml
1 U.S. gal weighs 13.3 lb (6.032 kg)
1 Imp gal weighs 15.95 lb (7.235 kg)
1 kg has volume 626.959 ml
1 litre weighs 1.595 kg

Dosages and concentrations of gas in air (25°C AND 760 MM PRESSURE)

BY VOLUME		WEIGHT PER VOLUME	
PARTS PER MILLION	PERCENT	[1]G/M³	LB/1 000 FT³
10	0.001	0.06	
50	0.005	0.31	
100	0.01	0.63	
159	0.016	1.00	
200	0.02	1.26	
500	0.05	3.14	0.20
1 000	0.10	6.29	0.39
2 543	0.254	16.00	1.00
20 000	2.0	125.85	7.86

[1]Ounces per 1000 cubic feet or milligrams per litre

CT fills a useful role in the fumigation field as an ingredient of mixtures, principally for grain fumigation. It is non-flammable in any concentration in air, and serves to reduce fire hazards of other fumigants, such as ethylene dichloride, carbon disulphide and acrylonitrile. Furthermore, the distribution of some liquid-type fumigants in a grain mass is aided by the presence of CT as one of the ingredients (Berck, 1958).

TOXICITY

Although, compared with other commonly used fumigants, CT is not very toxic to insects, it is now known to be extremely poisonous to human beings. Toxicity to humans is attributed mainly to extensive liver damage (Rouiller, 1964).

Human poisoning may be acute as the result of exposure to high concentrations but in practice it more often occurs as a chronic condition from comparatively low concentrations inhaled over extended periods of time. In recent years the threshold limits established by the American Conference of Governmental Industrial Hygienists have been progressively lowered until they are now at 5 parts per million (ppm) for continuous daily exposure to CT. This fumigant is now listed by the above agency in the category of industrial substances suspected of carcinogenic potential for humans (ACGIH, 1981).

There are two important considerations in CT poisoning. According to Rowe (1957) the vapours are not detectable by smell below 70 ppm in air. It should also be made known that CT does not "mix" well with alcohol:

"Persons who are prone to imbibe too heavily or too frequently show a considerably greater susceptibility to carbon tetrachloride poisoning" (Torkelson et al 1966)

RESIDUES IN FOODSTUFFS

Evidence is strong that CT is taken up physically and without chemical reaction in grain and grain products (Pepper et al, 1947; Lynn and Vorhes, 1957). Jagielski et al (1978) found residual CT in fumigated wheat and maize three months after treatment and a substantial proportion of this appeared in milled fractions, especially the bran. Small amounts (up to 0.03 mg/kg) could be detected in bread made from the treated flour. There is no positive evidence available on the presence or absence of CT metabolites in treated grain or other foodstuffs (Kenaga, 1967).

The toxicological significance of even small amounts of residual CT is not known, but the FAO Panel of Experts on Pesticide Residues in Food (FAD/WHO, 1980) suggested that guidelines be lowered below those previously recommended. They indicated that the following levels should be used as guide lines:

CEREAL GRAINS	50 mg/kg
MILLED CEREAL PRODUCTS (FOR BAKING AND COOKING)	10 mg/kg
MILLED CEREAL PRODUCTS (FOR CONSUMPTION WITHOUT COOKING)	1.01 mg/kg
BREAD AND OTHER COOKED CEREAL PRODUCTS	0.01 mg/kg

METHODS OF ANALYSIS

In the field determination of this fumigant, both the thermal conductivity analyser (Kenaga, 1958) and the interference refractometer can be used. It is important to point out that such methods are not applicable to CT in fumigant mixtures and should only be employed when CT is applied alone. Glass detector tubes are available for measuring low levels of CT in the 5 to 50 ppm range.

Residual CT in cereal grains, milled products and other stored foods can be determined by gas chromatography in the parts per thousand million range (Bielorai and Alumot, 1966; Heuser and Scudamore, 1969b). A cold extraction procedure for removal of CT from wheat and maize was found more effective than steam distillation (Scudamore and Heuser, 1973). Landen (1979) described a method for microassay of CT in drinking water and beverages.

CHLOROPICRIN

Chloropicrin is a powerful tear gas; it is one of the most toxic to insects of the fumigants commonly used today. It is sometimes added in small proportions to other fumigants, e.g., hydrogen cyanide and methyl bromide, to serve as a warning agent (see Chapter 3).

Although the tear gas effect of Chloropicrin is helpful in preventing persons from staying in dangerous concentrations during the fumigation process, it is also a handicap because fumigated commodities are unpleasant to handle for some time after fumigation. Even comparatively small amounts diffusing from the treated material may be extremely irritating. If it were not for this disadvantage, Chloropicrin would be useful for commodity treatments as it penetrates effectively into many materials.

Chloropicrin is also toxic to nematodes and certain fungi and it has found wide application as a soil fumigant.

Chloropicrin is corrosive to metals and care should be taken to protect metal surfaces and equipment during treatment.

T0XICITY

In humans, a concentration of 2.4 g/m^3 can cause death from acute pulmonary oedema in one minute (Hanslian, 1921). concentration us low as I ppm of Chloropicrin in air produces an intense smarting pain in the eyes, and the immediate reaction of any person is to leave the vicinity in haste. If exposure is continued, it may cause serious lung injury.

PROPERTIES OF CHLOROPICRIN
ALTERNATIVE NAMES: TRICHLORONITROMETHANE, NITROCHLOROFORM
STRONGLY IRRITATING TEAR GAS

CHEMICAL FORMULA	CCl_3 NO2
BOILING POINT	112°C
FREEZING POINT	-64°C
MOLECULAR WEIGHT	164.39
SPECIFIC GRAVITY	
GAS (AIR = 1)	5.676
LIQUID (WATER AT 4°C = 1)	1.651 at 20°C
FLAMMABILITY LIMITS IN AIR	Non-flammable
SOLUBILITY IN WATER	0.227 g/100 ml at 0°C
PERTINENT CHEMICAL PROPERTIES	Non-flammable; relatively inert; corrosive in presence of moisture
METHOD OF EVOLUTION AS FUMIGANT	By evaporation of liquid from pure compound or mixed with carbon tetrachloride. Sometimes dispersed as aerosol with methyl chloride as carrier.
COMMERCIAL PURITY	99%

Natural vapour pressure at different temperatures

0°C (32°F) 5.7 mm Hg
10°C (50°F) 10.37 mm Hg
20°C (68°F) 18.3 mm Hg
25°C (77°F) 23.8 mm Hg
30°C (86°F) 31.1 mm Hg
40°C (104°F) 51.1 mm Hg

Weights and volumes of liquid

1 lb (avdp) at 20°C has volume 274.7 ml
1 U.S. gal weighs 13.76 lb (6.243 kg)
1 Imp gal weighs 16.51 lb (7.489 kg)
1 kg has volume 605.69 ml
1 litre weighs 1.651 kg

Dosages and concentrations of gas in air (25°C AND 760 MM PRESSURE)

BY VOLUME		WEIGHT PER VOLUME	
PARTS PER MILLION	PERCENT	[1]G/M³	LB/L 000 FT³
20.1	0.00001	0.00067	
20	0.002	0.13	
50	0.005	0.34	
100	0.01	0.67	
149	0.015	1.00	
200	0.02	1.34	0.08
500	0.05	3.36	0.21
1 000	0.10	6.72	0.42
2 380	0.24	16.00	1.00
20 000	2.0	134.46	8.40

[1]Ounces per 1000 cubic feet or milligrams per litre

However, it is evident from the preceding statement that an individual will not willingly tolerate concentrations that are actually injurious (Torkelson et al, 1966).

EFFECT ON PLANT LIFE

Chloropicrin is extremely phytotoxic and plants exposed to its vapours are often completely destroyed. Even when added in small amounts to other fumigants for

warning purposes, it is likely to be toxic. For instance, methyl bromide containing small amounts of chloropicrin should not be used to fumigate plants, fruit or vegetables. When used for soil fumigation, it kills weed seeds and any living plant material present.

Nevertheless, it is possible to fumigate certain seeds with concentrations of chloropicrin toxic to insects without impairing germination (Hsin, 1959; Metzer, 1961; Solodovnik et al, 1963). Metzer recommended that seed treatments with this fumigant be conducted at temperatures lower than 27°C.

EFFECT ON PLANT PRODUCTS

Chloropicrin should not be used for the fumigation of fresh fruit or vegetables. It may be used on bagged or packaged plant products at atmospheric pressure if ample time is allowed for post fumigator aeration. The irritating vapours must be allowed to diffuse before the material is handled or consumed.

If chloropicrin is present in fumigated flour, it may have a bad effect on the baking quality, but this effect disappears once the material is fully aerated.

RESIDUES IN FOODSTUFFS

From available evidence it appears that the residue problem with this fumigant is confined to unchanged chloropicrin persisting in the treated foodstuff. There has been no indication of a significant residue from reaction products under normal conditions of fumigation, but the formation of inorganic nitrites and nitrosamines has been postulated (FAD/WHO, 1965a).

Getzendaner et al (1965) found that in dry beans and field peas fumigated with chloropicrin at 32 to 64 g/m³ for 24 hours at 25 to 26°C, residues were not in excess of 2 mg/kg after 4 days of aeration. With the same treatments most of the fumigant disappeared from maize, peas, beans, wheat flour, breakfast food and chicken feed but even after 3() days measurable amounts of chloropicrin, up to 9 mg/kg, persisted in wheat flour and up to 16 mg/kg in chicken feed. In the other materials the residues were less than 2 mg/kg. Flour containing 3.7 my/kg of chloropicrin before baking contained no measurable amounts afterwards. These authors point out that the physical state of the material being fumigated may have an important bearing on the amount of initial residue.

METHODS OF ANALYSIS

Methods for the determination of chloropicrin in air are given by Daecke and Kraul (1961), Berok and Solomon (1962a), and Ioanid et al (1963). The method used by Getzendaner et al (1965) for analysing chloropicrin residues in fumigated foods was sensitive from 0.1 to 100 mg/kg. Kanazawa (1963) and Berck (1965a) described gas chromatographic methods for determining this fumigant.

APPLICATION

Chloropicrin is commonly marketed in glass bottles containing 1 pound of the liquid. For safety, the bottles are packed individually in cans, which must be opened with a can opener. The fumigant is also available in steel cylinders containing 25 to 180 lb (11.5 to 81.5 kg) and is said to be noncorrosive to the containers if they are kept tightly closed.

Chloropicrin is difficult to vaporize at ordinary temperatures. In fumigation chambers it may be poured onto a crumpled jute (burlap) sack over which a powerful draught of air may be directed from a fan or blower when the fumigation starts. For volatilizing in flour and mill fumigation, it is sometimes mixed with methyl bromide or methyl chloride in a cylinder and discharged as a mist, from which the chloropicrin is rapidly volatilized.

Its application as a grain fumigant is described in Chapter lO and as a "spot" fumigant in Chapter 8.

PRECAUTIONS

As stated above, because of the tear gas effect, a person would be unable to remain in a dangerous concentration of chloropicrin for more than a few seconds. Great care should be taken to prevent unauthorized persons from approaching a fumigation site because the tear gas effect is so powerful that they may become temporarily blinded and panic-stricken, which, in turn, may lead to accidents. If it is necessary for the operator to expose himself to any concentrations of this fumigant, a canister especially designed for protection against "organic vapours and acid gases" should be fitted to the respirator.

For the use of chloropicrin as a warning gas, see Chapter 3.

DICHLORVOS (DDVP)

Dichlorvos, sometimes called DDVP, is the common name of dimethyl 2,2dichlorovinyl phosphate. Discussion of this material is pertinent to this manual, despite its high boiling point and low vapour pressure, because for certain usages it is discharged as a true gas to control insects in the open spaces of structures. It is also used as a contact insecticide, but a description of this type of application is outside the scope of this manual (Attfield and Webster, 1966).

PROPERTIES OF DLCHLORVOS
DIMETHYL 2,2-DICHLOROVINYL PHOSPHATE
ALTERNATIVE NAME : DDVP

CHEMICAL FORMULA	CCl2 = CHO.P0.(OCH3)2
BOILING POINT	120°C/14 mm
FREEZING POINT	Below -18°C
MOLECULAR WEIGHT	221
SPECIFIC GRAVITY	
GAS (AIR = 1)	7.6
LIQUID (WATER AT 15.6°C = 1)	1.44 at 15.6°C
DENSITY	0.142 kg per litre at 20°C
FLAMMABILITY LIMITS IN AIR	Non-flammable. Applied as fog or spray, flammability would be governed by solvent used
SOLUBILITY IN WATER	Slight (about 1%)

Pertinent chemical properties

Stable to heat. Undergoes hydrolysis in presence of water. Corrosive to black iron and mild steel. In absence of moisture, noncorrosive to aluminium, nickel and stainless steel. Non reactive with Teflon and polyethylene. Stable in presence of hydrocarbon solvents.

Method of evolution as fumigant

(a) By direct evaporation of liquid concentrate by means of heat.
(b) By volatilization from pressurised cylinders with inert Freon-type gases as carriers.
(c) By slow volatilization from resin strips (adult flies and mosquitoes only).
(d) By evaporation from resin cylinders (glasshouse fumigations).

Natural vapour pressure at different temperatures

20°C (68°F) 0.0108 mm Hg
10°C (50°F) 0.0041 mm Hg
30°C (86°F) 0.0272 mm Hg
60°C (140°F) 0.2985 mm Hg

Volatility (saturation – see also Table 2)

At 10°C, 51.5 mg/m³
At 20°C, 131 mg/m³
At 30°C, 318 mg/m³

Dosages and concentrations of gas in air (25°C AND 760 MM PRESSURE)

BY VOLUME		WEIGHT PER VOLUME	
PARTS PER MILLION	PERCENT	MG/M³	OZ/L 000 FT³
20.1		1.00	
1.0		10	
2		20	
5	O.005	50	O.05
10	0.01	100	0.1
15	0.015	150	0.15
20	0.02	200	0.2

[1]Ounces per 1000 cubic feet or milligrams per litre

Because of its low vapour pressure dichlorvos is unable to penetrate into materials. Therefore, it is of no value as a commodity fumigant.

Used as a fumigant, dichlorvos has found effective use at very low concentrations against houseflies, mosquitoes and mushroom flies. At higher concentrations it is effective against cockroaches and a wide range of stored product insects. It has been used successfully against moths and the cigarette beetle in tobacco warehouses. Recommendations for free space use are summarized in Schedule Q. Its application as A glasshouse fumigant is discussed in Chapter 12.

An important characteristic of dichlorvos is the fact that it hydrolyses slowly in the presence of water, and this process is accelerated in the presence of alkali and reduced in the presence of acid. An end product of hydrolysis may be dichloroacetic acid. Consequently, formulations and spaces treated with the insecticide may exhibit a vinegar-like odour if hydrolysis has occurred to any extent.

TOXICITY

The toxicity of dichlorvos to mammals is moderately high by ingestion, inhalation and absorption through the skin. It is a direct inhibitor of the enzyme cholinesterase but it is detoxified relatively quickly (Hayes, 1963). Although dichlorvos is a potential alkylating agent of DNA and RNA in vitro, this potential is apparently not realized in

vivo owing to the rapid degradation in mammals. Investigations for possible carcinogenic effects of dichlorvos have shown no increased incidence of tumours in experimental animals (Blair et al, 1976); this and other studies support the view that any potential for producing cancer in humans by dichlorvos would be extremely low (Anon, 1977; FAD/WHO, 1977). Studies for teratogenic effects have shown no serious changes in the progeny from treated animals (Schwetz et al, 1979; Wrathall et al, 1980).

On the other hand, insect cholinesterase inhibited by dichlorvos is not readily reactivated, and in consequence intoxication is irreversible (O'Brien, 1960). This reaction is typical of the dimethyl phosphate insecticides.

EFFECT ON PLANT LIFE

Dichlorvos in the concentrations used for control of glasshouse pests is not generally phytotoxic. Pass and Thurston (1964) listed 42 plants, including 20 flowering plants, which were not injured by exposure for 15 hours at 20°C to dichlorvos vapours generated at the rate of 1.5 fluid ounces (U.S.) of 90 percent concentrate per 10 000 cubic feet (eriaivalent to 204 mg/m³ of dichlorvos vapour which in full concentration, would be above the saturation point of 131 mg/m³ at this temperature). The only adverse effect noted was a slight discoloration or fading of chrysanthemum blooms. Glancey and Naegele (unpublished data, 1965) also reported that dichlorvos was safe to use for the insecticidal fumigation of glasshouse plants, except that one variety of chrysanthemum (Shasta) showed severe leaf burning. However, Harnlen and Henley (1979) were unable to obtain satisfactory control of green peach aphid and two spotted spider mite on a number of indoor ornamental plants in continuous room fumigation tests. They found that a multiple fumigation treatment at seven-day intervals with dichlorvos impregnated polyvinyl chloride resin strips in polyethylene hags was more effective, but some injury to the plants did occur.

RESIDUES IN FOODSTUFFS

The amount of dichlorvos absorbed can vary considerably with different food materials. In measurements of residues absorbed in prepared meals during disinfestation of aircraft it was noted that margarine contained three times as much as the cooked meal and the beverages approximately one tenth as much (Dale et al, 1973).

Table 13 summarizes some information on the persistence of dichlorvos in certain foodstuffs exposed to the insecticide when discharged as a vapour. Dichlorvos breaks down rapidly after application, so the residues decline to very low levels during storage and shipment. The higher the temperature and moisture content of the material or its environment, the more rapid is the breakdown. In studies on the use of dichlorvos in mills at temperatures ranging from 18 to 22°C, dichlorvos residues degraded within a period of 2 4 weeks, depending on the kind of product treated (Wirthgen and Raffke, 1979).

It may be concluded that, when dichlorvos vapour is applied to closed spaces containing foodstuffs, rapid hydrolysis leads to the disappearance of significant residues of this chemical in a very short time.

The toxicological evaluation of dichlorvos is that 10 mg/kg in the diet, equivalent to 0.5 mg/kg of body weight per day, is the level that will cause no toxicological effect; the estimated acceptable daily intake for man is 0 to 0.004 mg/kg of body weight (FAD/WHO, 1978b).

METHODS OF ANALYSIS

Determination of Vapours

Concentrations of dichlorvos in confined spaces can be measured by several different methods including cholinesterase inhibition (Webley and McKone, 1963; Heuser and Scudamore, 1966), calorimetric (Bracha et al, 1963; Mukherjee et al, 1973), titrimetric and bioassay procedures (Muthu et al, 1973). Gas chromatographic methods can provide rapid, specific and sensitive determinations (Bond et al, 1972; Bryant and Minett, 1978). Samples from the atmosphere can be taken directly by gas syringe and injected into a gas chromatograph or they may be collected by passing a known volume of air through glass tubes packed with potassium nitrate and taken to a gas chromatograph, as described by Bryan and Minett (1978).

TABLE 13. – RESIDUES OF DICHLORVOS IN FOOD

	INSECT SPECIES	CONCENTRATION DICHLORVOS VAPOUR		TEMPERATURE	DURATION OF EXPOSURE	RESIDUE DICHLORVOS OBSERVED
		APPLIED	SATURATION			
		MG/M³		°C		MG/KG
Cocoa beans	Ephestia elutella (Hbn.)	0.04 to	131	18	54 days	Whole beans, surface layer near strips, 0.02
in sacks		0.05				
in store	(moths only)	(from resin strips)				Whole beans, middle of top sacks, 0.01
Meat	–	*05	84	13–15	24 hours	Minced meat 0.33 Bacon 0.32 Steak 0.23 Fat 0.17
Mushrooms (a)	Megaselia halterate (Wood)	218	131	17–20	–	Nil 3 hours after exposure
Mushrooms (b)	Sciarid and Phorid flies	2120	131	17–20 ?	4 hours	Nil 24 hours after exposure with 1,2 or 3 consecutive applications

* Concentration of 0.5 mg/m³ lasted for 30 minutes, no vapour detectable after 3 hours.
SOURCES: Schulten and Kuyken (1966) for cocoa beans: Miller and Aitken (1965) for meat:

Hussey and Huges (1964) for mushrooms (a); Snetsinger and Miner (1964) for mushrooms (b).

Determination of Residues

The dichlorvos remaining in food material can be extracted and coricentrated by using appropriate solvents for the type of food concerned. Details of methods for such extractions with subsequent analysis by gas chromatography are given by various authors (Abbott et al, 1972; Bond et al, 1972; 1 a Hue et al, 1975; Schmidt and Wohlgemuth, 1979).).

APPLICATION

A simple method of vaporizing dichlorvos as a fumigant for closed spaces is to place the required amount of liquid concentrate in an open dish or beaker and heat it on a hot plate. An ordinary electric fan or blower placed close to the source may be used to disperse the vapours to effect even distribution.

Jensen et al (1961) described a mechanical system for dispersing known amounts of dichlorvos. This system was originally designed for fly and mosquito control in aircraft, but would also be suitable for use in a wide variety of structures requiring routine applications at regular or intermittent intervals.

Dichlorvos is also available in cylinders mixed, up to 20 percent by weight, with Freon-type inert propellants. This method of vaporization is very convenient but is more expensive.

For the control of flies and mosquitoes attacking humans and animals in houses and buildings, resin strips each containing about 20 percent dichlorvos by weight are extremely effective. By slow vaporization these strips will maintain concentrations up to 0.44 mg/m in a tightly closed room at 23.3°C. Concentrations of 0.15 to 0.25 mg/m^3 are fully effective against flies and mosquitoes within 30 minutes. Use of these strips is not an effective method for controlling cockroaches and stored-product insects.

The application of this chemical as a fumigant in glasshouses is discussed in Chapter 12.

Dosages and Concentrations

In the literature and in trade publications, dosages of dichlorvos are expressed in different ways. Sometimes both the metric and British systems are used in the same prescription. Equivalents of some of the more common methods of expressing dosage are given in the table of properties of dichlorvos.

PRECAUTIONS

Concentrations Toxic to Humans

According to the threshold limit set by the American Conference of Governments I Industrial Hyigienists (ACGIH, 1981), the maximum permissible concentration of daily exposure to humans is 1 microgram (µg) per litre (1 mg/m^3). Hayes (1963) stated that tests have shown that men can withstand brief exposure to air concentrations at least as high as 6.9 µg/l without clinical effect or depression of blood cholinesterase; intermittent exposure totalling 5 hours daily at a concentration of ().5 µg/l produces no clinical effect and no effect on red cell cholinesterase, but does cause a gradual moderate reduction of plasma cholinesterase.

Zavon and Kindel (1966) studied the effect of prolonged exposure, up to six months, on humans exposed to the low concentrations of dichlorvos not exceeding 0.01 µg/l of air generated from resin strips of the type marketed for control of flies and mosquitoes in houses. They concluded that the handling and use of the resin vaporizers, under recommended conditions, would be unlikely to result in adverse effects among persons so exposed.

Durham et al (1959) studied the effects of exposure to dichlorvos in human volunteers, not wearing respirators, who worked in a tobacco warehouse where the insecticide was applied at regular intervals to control insects. They concluded that the conditions would be safe for workers where dichlorvos was applied twice a week or less at 70 mg/m^3.

Dichlorvos is easily absorbed through the skin and if even small amounts of formulations containing this insecticide are spilled on the clothes or body, these may produce very serious results requiring medical treatment (Hayes, 1963).

Respiratory Protection

When dichlorvos is being applied as a fumigant indoors or in glasshouses, those applying the insecticide must wear an industrial-type respirator (gas mask) with a filter-type canister which gives full protection against organic vapours and acid gases (see Chapter 3 Table 8). A small cartridge-type respirator of the kind described in Chapter 3 does not give adequate protection when dichlorvos is being used for industrial purposes.

FIRST AID

The following is a summary giving the salient information on first aid and subsequent treatment by a physician for poisoning or suspected poisoning by dichlorvos. The manufacturers of this insecticide supply special booklets on first aid and treatment, with detailed information for physicians arid a list of important precautions to be taken during formulation.

Warning symptoms include weakness, headache, tightness in the c-nest, blurred vision, non-reactive pin-point pupils, salivation, sweating, nausea, vomiting, diarrhoea and abdominal cramps.

In all cases of suspected poisoning, remove the patient from further exposure to the poison, restore breathing anti get medical help immediately. Details of the accident, including the name of the poison, the quantity involved anti how the accident occurred, i.e. by inhalation ingestion or by skin contact, should be supplied to the doctor or hospital emergency centre.

If dichlorvos has been swallowed, induce vomiting (in fully conscious patients only) by stroking or tickling the back of a patients throat with a finger. Do not give salt water as this may involve serious risk.

If the patient has been poisoned by external contact with dichlorvos, remove contaminated clothing immediately and wash the skin thoroughly with soap and water; use plenty of water in rinsing. If dichlorvos gets into the eyes, wash it out immediately using running water for at least 10 minutes.

Emergency treatment personnel should be aware that atropine is the antidote of choice for treatment of dichlorvos poisoning. However, atropine should never be administered unless warning signs of intoxication appear.

Information for Physicians

Regardless of the route of absorption, dichlorvos inactivates the cholinesterase enzymes of both the blood and tissues. Intoxication produces signs and symptoms of excessive cholinergic stimulation. Diagnosis may be substantiated by plasma and red cell cholinesterase analyses using the Michel method (J. Lab. Clin. Med., 34: 1464, 1949) or the Ellman colorimetic method (Biochem. Pharmacol., 7: 88, 1961). Atropine should be given intravenously in doses of I to 2 mg; if cyanosis is present, the atropine should be given intramuscularly while simultaneously initiating measures to improve ventilation. Atropine administration should be repeated at 5- to 10- minute intervals until atropinization is complete. A mild degree of atropinization should be maintained for at least 24 hours and in severe cases for at least 48 hours. Morphine, adrenaline, tranquilizers and similar substances are contraindicated.

Complete recovery may be anticipated even in those cases where severe poisoning has occurred and after many hours of artificial respiration. A patient should be watched continuously for 48 hours when the exposure has been severe enough to produce symptoms. No further exposure to any Organo phosphorous or carbamate insecticide should be allowed until the blood cholinesterase, as determined by blood tests, has returned to normal.

SULPHURYL FLUORIDE

Sulphuryl fluoride has been developed as an effective fumigant for controlling dry wood termites. This gas has outstanding dispersion and penetrating qualities which permit it to infiltrate termite tunnels and crevices and destroy the insects. Sulphuryl fluoride does not escape through plastic sheets used in structural fumigation as rapidly as methyl bromide or other organic fumigants. Because this gas is odourless, chloropicrin, discharged separately, is recommended as a warning agent.

PROPERTIES OF SULPHURYL FLUORIDE

ODOUR	None
CHEMICAL FORMULA	SO_2F_2
BOILING POINT	-55.2°C
MELTING POINT	-120°C
MOLECULAR WEIGHT	102.06
SPECIFIC GRAVITY	
GAS (AIR = 1)	2.88
LIQUID (WATER AT 4°C = 1)	1.342 at 4°C
LATENT HEAT OF VAPORIZATION	79.5 BTU/lb at -55.2°C
FLAMMABILITY LIMITS IN AIR	Non-flammable
SOLUBILITY IN WATER	0.075 g/100 g at 25°C
PERTINENT CHEMICAL PROPERTIES	Noncorrosive, relatively unreactive and harmless to wide variety of household materials
METHOD OF EVOLUTION AS FUMIGANT	From steel cylinders under natural pressure
COMMERCIAL PURITY	99%

<u>Natural vapour pressure at different temperatures</u>

10°C (50°F) 9 150 mm Hg
25°C (77°F) 13 442 mm Hg

<u>Weights and volumes of liquid</u>

1 lb at 4°C (39.2°F) has volume 338 ml
1 U.S. gal weighs 11.17 lb (5.069 kg)
1 Imp gal weighs 13.42 lb (6.087 kg)
1 kg has volume 745.1 ml
1 litre weighs 1.342 kg

Dosages and concentrations of gas in air (25°C AND 760 MM PRESSURE)

BY VOLUME		WEIGHT PER VOLUME	
PARTS PER MILLION	PERCENT	[1]G/M³	LB/L 000 FT³
25	0.0005	0.0228	
20	0.002	0.091	
50	0.005	0.228	
100	0.01	0.456	
200	0.02	0.91	
239.6	0.024	1.00	0.062
500	0.05	2.278	0.142
1 000	0.10	4.556	0.285
3 833.2	0.383	16.00	1.00
20 000	2.0	91.12	5.695

[1]Ounces per 1000 cubic feet or milligrams per litre

TOXICITY

Although highly toxic to humans acutely exposed, there have been few reports of accidental poisoning. This may be due to the fact that sulphuryl fluoride aerates very rapidly from fumigated buildings and also because, in its present usage, it is only applied by properly qualified operators. Its mammalian toxicity by inhalation, is about equal to that of methyl bromide.

Sulphuryl fluoride is generally very toxic to all postembryonic stages of insects (Kenaga, 1957b; Bond and Monro, 1961), but the eggs of many species are extremely resistant. It has been suggested that this resistance is largely due to the impenetrable nature of the eggshell layers to this chemical (Outram, 1967).

EFFECT ON MATERIALS

The effect of sulphuryl fluoride on materials found in houses and on plants and products has been summarized by Gray (1960) as follows.

"In laboratory and field tests, sulphuryl fluoride has shown no objectionable colour, odour, or corrosive reactions to photographic supplies, metals, paper, leather, rubbers, plastics, cloths, wallpapers or any other of a large number of articles fumigated.

"Sulphuryl fluoride has little or no effect on the germination of weed and crop seeds; however, it is injurious to green plants, vegetables, fruits and tubers. Sulphuryl

fluoride is sorbed less than methyl bromide in wheat, wood flour and many other materials."

Meikle and Stewart (1962) found that in fumigation with this compound the residual fluorides in foodstuffs are low except in certain proteinaceous foods which have a solvent system, such as fat in cheese and meat.

At the present time the manufacturers of a proprietary fumigant of sulphuryl fluoride (Dow Chemical Company, 1963) state specifically:

"Under no conditions should sulphuryl fluoride be used on raw agricultural food commodities, or on foods, feeds or medicinals destined for human or animal consumption. Do not use on living plants."

METHODS OF ANALYSIS

Determination of Vapours

Gross determination of concentrations of sulphuryl fluoride may be made with the thermal conductivity meters described in Chapter 4. fly using known concentrations of the gas, these instruments may be calibrated to read the gas concentration in terms of oz/1000 ft^3. For instruments of known calibration for methyl bromide, A straight-line relationship exists for reading concentrations of sulphuryl fluoride. For example, a reading of 7 g/m^3 is equivalent to 4 9 of sulphuryl fluoride/m3. The accuracy of thermal conductivity meters decreases with decreasing concentrations to the point where the readings become unreliable at concentrations of sulphuryl fluoride below 4 g (approximately 960 ppm)/m3. However, this is sufficiently accurate for normal commercial fumigation practices. Heuser (1963) described two analytical methods suitable for sulphuryl fluoride determinations under field conditions. These methods would also be useful for checks on the efficiency of the thermal conductivity analysers. For monitoring residual concentrations of this fumigant during the aeration of buildings, the manufacturers are careful to point out that the halide lamp described above under methyl bromide is not suitable for sulphuryl fluoride. It is recommended that a special device developed by them be used (Gray, 1960; Dow Chemical Company, 1963). The infra-red analyser described in Chapter 3 can be used for sensitive analysis of this fumigant. The Dow Chemical Company now recommends a modified portable SO2 analyser for excellent accuracy, fast measurements and low cost.

APPLICATION

Sulphuryl fluoride for termite control is most often applied to residences or other buildings, which are covered with gas-proof sheets. The fumigant is discharged directly from siphoned cylinders under its own vapour pressure. No auxiliary source of heat is required. The cylinders are placed on platform type scales and the dosage read directly by change in weight. Metering devices are not safe and are not recommended.

This fumigant will discharge through 0.3 cm (inside diameter) thick-walled polyethylene plastic tubing at the rate of 2 to 2.5 kg per minute.

For the purpose of monitoring gas concentrations so as to provide efficient and economical treatments to control termites in buildings, the manufacturers of sulphuryl fluoride supply special guide charts. These charts give factors for calculating the variables likely to be encountered during a fumigation and are best used in conjunction with the thermal conductivity analyser (Stewart, 1966).

PRECAUTIONS

Concentrations Toxic to Humans

The threshold limit for sulphuryl fluoride is 5 ppm for repeated eight hour exposures five days per week (ACGIH, 1981). The short-term exposure limit should not exceed 10 ppm (see Chapter 3, Table 7).

Respiratory Protection

In proper practice with this material there is no need for the operator to be exposed to the fumigant. In planning a fumigation, care should be taken to eliminate the possibility of anyone breathing any concentration. This is not only good general fumigation practice, but is also particularly important with sulphuryl fluoride because the standard respirator canister affords protection for a very short time, owing to the nature of the gas. According to instructions on the label issuer) by the manufacturer, a special canister designed for sulphuryl fluoride and other acid gases is required.

Protection from concentrations up to 32 g/m^3 for 15 minutes can be obtained with the appropriate canister. For higher concentrations of sulphuryl fluoride, or for longer periods of time, air-supplied or self-contained breathing apparatus should be used.

FIRST AID

The manufacturers of sulphuryl fluoride supply a booklet giving detailed recommendations for first aid, with suggestions to the physician.

The following condensed information on first aid is supplied on the manufacturer's label:

"Send for a doctor in case of accident. If a person should be overcome from breathing this gas, immediately place patient in fresh air, face downward, with head slightly below level of lungs. Keep warm. If breathing stops, give artificial respiration.

Note to physician: First symptoms expected are those of nausea, respiratory irritation and central nervous system depression; excitation may follow. Treat symptomatically. There is no known antidote."

ACRYLONITRILE

Owing to its low limits of flammability, acrylonitrile is never used alone as a fumigant but always in a mixture with another suitable material, which reduces the possibility of fire or explosion. A commonly used formulation was made up of acrylonitrile 34 percent and carbon tetrachloride 66 percent by volume. In practice, therefore, the effects of acrylonitrile fumigation were dependent on the action of the mixture.

Acrylonitrile itself has a comparatively high boiling point. When the mixture is used in atmospheric fumigations, it is necessary to hasten evaporation by pouring the liquid over a piece of jute (burlap) or similar cloth placed in an evaporating pan near the ceiling, and, if possible, in the air stream from a nearby circulating fan or blower.

The mixture of acrylonitrile and carbon tetrachloride has been found useful for the following purposes:

1. As a "spot" fumigant in mill, bakery and processing machinery.

2. For use in atmospheric chambers for fumigating tobacco (Tenhet, 1954; Childs and Overby, 1967), nutmeats (shelled nuts) and dates. It does not penetrate into certain closely packed materials as readily as methyl bromide and therefore is not usually recommended for use with flour and other milled products.

3. For the vacuum fumigation of tobacco (Tenhet, 1957).

4. For fumigation of buildings to control dry wood termites.

PROPERTIES OF ACRYLONITRILE
ALTERNATIVE NAMES: VINYL CYANIDE, CYANOETHYLENE, PROPENE NIT RIFE

ODOUR	Penetrating odour, bitter taste
CHEMICAL FORMULA	CH_2 : CH.CN
BOILING POINT	77°C
FREEZING POINT	–82°C
MOLECULAR WEIGHT	53.06
SPECIFIC GRAVITY	
GAS (AIR = 1)	1.83
LIQUID (WATER AT 4°C = 1)	0.797 at 20°C
FLAMMABILITY LIMITS IN AIR	3 to 17% by volume
SOLUBILITY IN WATER	7.5 g/100 ml at 25°C
PERTINENT CHEMICAL PROPERTIES	Flash point (open cup) 4°C
METHOD OF EVOLUTION AS FUMIGANT	By evaporation from liquid. Because of flammability mixed in practice not more than 34%, with carbon tetrachloride 66%

<u>Natural vapour pressure at different temperatures</u>

0°C (32°F) 33.0 mm Hg
10°C (50°F) 54.8 mm Hg
20°C (68°F) 87.5 mm Hg
25°C (77°F) 105 mm Hg
30°C (86°F) 140 mm Hg
40°C (104°F) 214 mm Hg

<u>Weights and volumes of liquid</u>

1 lb (avdp) at 20°C has volume 569
1 U.S. gal weighs 6.64 lb (3.014 kg)
1 Imp gal weighs 7.97 lb (3.615 kg)
1 ml 1 kg has volume 1 254.7 ml
1 litre weighs 0.797 kg

<u>Dosages and concentrations of gas in air</u> (25°C AND 760 MM PRESSURE)

BY VOLUME		WEIGHT PER VOLUME	
PARTS PER MILLION	PERCENT	[1]G/M³	LB/L 000 FT³
20	0.002	0.04	
50	0.005	0.11	
100	0.01	0.22	
200	0.02	0.43	
461	0.046	1.00	
500	0.05	1.10	0.07
1 000	0.10	2 17	0.135
7 373	0.74	16.00	1.00
20 000	2.0	43.40	2.71

[1]Ounces per 1000 cubic feet or milligrams per litre

TOXICITY

Acrylonitrile is highly toxic to humans when ingested, inhaled or absorbed through the skin. It exhibits many of the effects of hydrogen cyanide and is a severe skin and eye irritant. There are indications that acrylonitrile is associated with certain types of cancer in workers exposed over long periods of time (Tierney et al, 1979) . A threshold limit value of 2 ppm was proposed in 1950 for adoption by the American Conference of Governmental Industrial Hygienists.

Acrylonitrile is very toxic to insects. It was found to be the most toxic of the more important fumigants used against several stored products insects (Bond and Monro, 1961; Lindgren et al, 1954; Harein and Soles, 1964; Rajendran, 1980). (See also Chapter 14, Table 16.) The present use of acrylonitrile as a grain fumigant is under review in some countries because of suspected toxic effects to humans. Consequently, its future use may be limited or prohibited on this account.

EFFECT ON PLANT LIFE

<u>Seeds</u>

Acrylonitrile alone or in mixture with carbon tetrachloride is reported as not affecting the germination of a wide range of vegetable, cereal and flower seeds (Glass and Crosier, 1949; Lindgren et al, 1954) . However, C.H. Richardson (1951) found them both detrimental to the germination of m a i z e .

Plants and Trees

Acrylonitrile is highly toxic to nursery stock and growing plants. It is not recommended as a plant fumigant either alone or in mixture.

EFFECT ON PLANT PRODUCTS

Fresh Fruit

Acrylonitrile seriously damages many fresh fruits (Claypool and Vines, 1956) .

Vegetables

Pradhan et al (1960) in India found that a 1: 1 mixture by volume of acrylonitrile and carbon tetrachloride could be employed to control the potato tuber moth, Phthorimaea opercullela (Zell.), in stored potatoes without injuring the tubers.

Cereals

Acrylonitrile-carbon tetrachloride mixtures have been recommended fur the control of insects in stored grain (Cotton and Young, 1943; Ruppel et al, 1960) .

RESIDUES IN FOODSTUFFS

There is little information available on the residues remaining in materials treated with acrylonitrile. The fumigant sorbed by several commodities and desorption may require many days, depending on the type of commodity and the aeration conditions. Residual fumigant was found to desorb most rapidly from groundnuts and maize and slowest from wheat (Dumas and Bond, 1977). In admixture with carbon tetrachloride was found to disappear from spelled walnuts more rapidly than carbon tetrachloride (Berck, 1960). Residues of both fumigants were lower following vacuum fumigation for three hours than after treatment at atmospheric pressure for 18 and 48 hours .

METHODS OF ANALYSIS

A number of procedures using gas chromatography that will give rapid and precise analysis of acrylonitrile have been developed. Gawel (1979) described a headspace gas-chromatographic method for determination of concentrations down to 0.005 mg/kg, and Dumas and Bond (1977) gave a method for extraction of residual acrylonitrile from food materials.

Detector tubes described by Dumas and Monro (1966) may be used for field determinations at both fumigation and threshold limit concentrations. The presence of carbon tetrachloride in admixture has no effect on the readings for acrylonitrile.

APPLICATION

Owing to the high boiling points of the two components of the acrylonitrile-carbon tetrachloride mixture, special provision has to be made for rapid volatilization in atmospheric fumigation. Childs and Overby (1967) described the use of cotton rope wicks drawn through the bottom of a shallow steel pan. At the beginning of the treatment, liquid fumigant is poured into the pan and a fan blows air over the wicks for the time needed to complete volatilization.

MINOR FUMIGANTS

In addition to the more important fumigants discussed above there are others with limited use, often for some specific application. The compounds listed in Chapter 2, fable 1 for reference purposes and which are not further discussed, are ethyl formate, methyl formate and paradichlorobenzene.

Besides the fumigants given in Table 1, there are a few compounds that should be mentioned; these either show promise for future applications, or have a restricted use at present.

ACETALDEHYDE

Acetaldehyde is a naturally occurring volatile compound that is toxic to insects as well as certain fungi, bacteria and yeasts. Tests on fruit and vegetables have shown that it can be used to control some insects, such as aphids and thrips, without undue injury to the fresh produce (Aharoni et al, 1979, 1980). Concentrations up to 3 percent for 30 minutes have been applied to apples as a fungicidal treatment without causing injury to the fruit (Stadelbacher and Prasad, 1974).

The boiling point of acetaldebyde is 21°C, it has a characteristic pungent odour and is flammable at concentrations of 4 percent or greater. Acetaldehyde is less toxic to mammals than other commercial fumigants, such as ethylene dibromide. It has a narcotic action on the nervous system and causes irritation to the eyes and mucous membranes. Large doses may cause death by respiratory paralysis. This compound is suspected of having carcinogenic activity in humans (Obe et al, 1979); however, it is not likely to be hazardous as a residue on fresh produce because it does not accumulate in tissues (Fidler, 1968).

Plant tissues may absorb acetaldehyde but it is metabolized to acetic acid, ethanol and carbon dioxide. Acetaldehyde occurs naturally in fruit and vegetables, it is used as a flavouring agent and has been registered as a food additive in the United States. This compound and other naturally occurring volatile compounds, such as ethyl formate, may have some potential as future replacements for fumigants that leave harmful residues.

AZ0BENZENE

This compound (boiling point 293°C) is a crystalline solid which has proved useful in the past for the control of mites in greenhouses. It acts as a vapour formed by heating the pure crystals by means of steam pipes, hot plates or lamps; it is also evolved by igniting a powder in a pressure fumigator. Many glasshouse plants and blooms are tolerant, but there has been some discoloration of red flowers (Pritchard, 1949). Flowers of the African violet (Saintpaulia) are reported to be susceptible to damage (Brown, 1951).

CHL0R0F0RM

Chloroform (boiling point 61°C) is not highly toxic to insects but it has shown considerable promise as a constituent of liquid-type fumigants, in which it serves as a carrier for other more toxic ingredients, such as ethylene dibromide and carbon disulphide. Chloroform is non-flammable when mixed in air in any proportion. However, it is listed as being a compound which is "suspect of inducing cancer" by the American Conference of Governmental Industrial Hygienists (ACGIH, 1981).

DICHLORONITROETHANE

This fumigant (boiling point 124°C) was introduced some years ago and appeared useful for treating grain, other stored products and soil. It gives warning by odour and irritation of the eyes. It may be strongly corrosive to metals in moist atmospheres.

ETHYLENE CHLOROBROMIDE

Ethylene chlorobromide is effective against the oriental fruit fly, but it is not as toxic as the closely allied ethylene dibromide (Balock and Lindgren, 1951). It has a lower boiling point than EDB. The effect of this fumigant on fruit and plant material is similar to that of EDB. It has not come into general use, although it has been adequate in many fields of application for which EDB is also suited (Benschoter, 1960, 1963; Wolfenbarger, 1962; Sinclair et al, 1964; Richardson and Roth, 1966).

METHYL ALLYL CHLORIDE

This gas, also called methallyl chloride, has been suggested as a grain fumigant and has been used experimentally in mixtures with other fumigants. In laboratory tests it has ranked above carbon disulphide and ethylene dichloride against eight species of stored-product insects (Lindgren et al, 1954) and it is considerably more toxic than carbon tetrachloride, although less toxic than ethylene dibromide. Methallyl chloride has a boiling point of 72°C and is non-flammable in concentrations toxic to insects. In field trials in Russia it has shown promise as a fumigant for cereal grains and pulses and is significantly less expensive to apply than chloropicrin and methyl bromide (Cherkovskaya, 1963, 1966). Methallyl chloride also shows promise for fumigation of individual sacks of grain (Taylor, 1975).

METHYLENE CHLORIDE

Methylene chloride has been found useful as an ingredient of fumigant mixtures (see Chapter 7). It is non-flammable and has a boiling point of 40.2°C. In itself it is toxic to insects, but ranks low in toxicity in comparison with other commonly used materials (Back and Cotton, 1935).

NICOTINE

Nicotine (boiling point 247°C), vaporized in different ways, was formerly used extensively as a glasshouse fumigant. The most convenient method of volatilizing it is by the use of pressure cans; these are ignited to send off dense clouds of smoke containing the vapours of nicotine. In a glasshouse, it was found that the nicotine concentrations fell off rapidly and little or none remained one hour after discharge (Richardson et al, 1943a). When the nicotine was evaporated slowly, the concentration was maintained only as long as evaporation continued and the introduction of fumigant was equal to the loss through leakage(Blackish, 1953). Delicate flowers and tender shoots may be injured by nicotine applied in any way.

Nicotine fumigation in glasshouses has been largely replaced by the aerosol technique described in Chapter 12. Nevertheless, it is still used under certain conditions, for example when convenience in application is important.

PROPYLENE DICHLORIDE

In empty containers, this compound (boiling point 96.4°C) compares favourably with many other fumigants in toxicity to insects. It has been tried as a grain fumigant, usually in mixture with carbon tetrachloride, but so far has not been widely adopted (Cotton, 1963).

SULPHUR DIOXIDE

Sulphur dioxide (SO2) should be mentioned if only to point out its disadvantages. It is the oldest fumigant known to man (Cotton, 1963), having been used from time immemorial by burning sulphur.

Nowadays it is sometimes used as an ingredient of liquid grain fumigants. Intrinsically it is quite toxic to insects. It also serves as a warning gas in these mixtures on account of its intensely irritating properties to humans. It is rapidly sorbed by any material undergoing treatment; it has a deleterious effect on grain and flour and is highly corrosive to metals (Cotton, 1963).

METHYL CHLOROFORM (1,1,1 - TRICHLOROETHAME)

This compound has been tested as a possible substitute for carbon tetrachloride; it is slightly more toxic to insects than the latter but less toxic than ethylene dichloride. Its

boiling point (74°C) and volatility are very similar to those of carbon tetrachloride. The vapour density of methyl chloroform is sufficiently greater than air that effective penetration into grain masses can be expected. When used as a 1 : 1 mixture with ethylene dichloride, an enhanced toxic effect was noted and the two compounds were found to interact physically to affect the distribution of each other in a grain bulk (UK, 1978).

Tests have indicated that residues of methyl chloroform should not be a toxic hazard in fumigated grain; no adverse effects were noted on bread made from fumigated wheat and virtually no residue could be detected in the loaves (UK, 1978).

Methyl chloroform is less toxic to humans than several other halogenated hydrocarbons of comparable function, including carbon tetrachloride. Animal and human toxicological data indicate that this compound should have little potential for producing permanent organic injury in humans, provided anaesthetic concentrations, sufficient to depress the respiratory centre, are not exceeded (Steward et al, 1969). The threshold limit value is 350 ppm (ACGIH, 1981). For the detection of low concentrations of methyl chloroform, the halide leak detector and glass detector tubes may be used.

CARBON DIOXIDE

Carbon dioxide (CO2) is an ingredient of our normal atmosphere and is not to be considered as a poisonous fumigant in the ordinary sense. Nevertheless, it has an important role in insect control (see Chapter 11).

7. FUMIGANT MIXTURES

Fumigants are sometimes marketed in mixtures with other compounds.

There are a number of practical reasons for combining fumigants, the more important being:

1. The flammability risk of the toxic ingredient is reduced or prevented altogether by the addition of another chemical. Examples are the addition of carbon dioxide to ethylene oxide or methyl formate and of carbon tetrachloride to acrylonitrile or carbon disulphide.

2. With liquid-type fumigants in grain fumigation, mixtures may be made to provide ingredients whose vapours have differing rates and patterns of diffusion. After the liquid has been applied to the surface the ingredients evaporate. The distance the ingredients diffuse downward depends largely on the extent to which they are sorbed by the grain. It may, therefore, be necessary to have various types of ingredients in the mixture to kill insects at various depths and locations in the grain (Kenaga, 1957a). An example is a mixture of ethylene dibromide, ethylene dichloride, carbon disulphide and carbon tetrachloride, which is used for grain fumigation in farm storage units and country elevators.

Similarly with gaseous fumigants, mixtures may be used to obtain complementary advantages. Phosphine is used in combination with methyl bromide in treatments of materials such as oil-seed expeller; the phosphine penetrates deeply into the material while the methyl bromide gives more control on the outer surfaces (Wohigemuth et al, 1976).

3. A highly volatile fumigant such as methyl bromide may diffuse downwards too rapidly, so that the upper part of a load of infested goods may not receive an adequate insecticidal treatment. Another less volatile fumigant, such as ethylene dibromide, is added to ensure that the material at the top is properly fumigated. A mixture of this type may be useful under tropical conditions when commodity temperatures may range as high as 38°C (Majumder and Muthu, 1964).

4. The principal toxic ingredient may be diluted so that its distribution becomes more uniform. Carbon tetrachloride, though only moderately insecticidal in itself, aids in the distribution of other fumigants, such as ethylene dibromide, which does not diffuse well through masses of grain (Berck, 1958).

Although fumigant mixtures are very useful for many types of application, especially for the treatment of grain in bulk and for local or spot fumigations, it should be pointed out that their use involves certain complications. As indicated above, the ingredients may settle out in different parts of the fumigation system. This may result in a situation whereby the more toxic material is acting against one part of the insect

population while the less toxic ingredients are acting against the remainder. Erratic results may thus be recorded unless full provision is made to allow time for the less toxic materials to exert their maximum effect.

Another objection, which is possibly more serious, is the fact that commonly used methods of field analysis of vapours, such as the thermal conductivity analyses, will not differentiate between the components of the mixture so that is not practicable to attempt to keep a check on the effective distribution of the toxic ingredients. Any reading taken with this type of instrument is meaningless under these conditions. A gas chromatograph or an infra-red analyser would provide the necessary information in the field, or samples could be brought to the laboratory for immediate analysis. Kenaga (1957a) has suggested the use of the mass spectrometer for the analysis of mixtures but this expensive instrument would have to be used in the laboratory.

Some fumigants that have been Found effective in mixtures are discussed below. They are given in the alphabetical order of the more insecticidally active ingredient of the mixture. The proportions of fumigants in a liquid state at normal temperatures are usually expressed in terms of volume. Mixtures containing volatile ingredients, such as methyl bromide, are expressed by weight of the components.

ACRYLONITRILE

Because of its flammability, acrylonitrile is never applied alone but always in admixture with non-flammable materials. Mixed with carbon tetrachloride it has been used as a local fumigant and for the fumigation of tobacco. Mixed with chloroform or methylene chloride it has been employed with some success for fumigating buildings against dry wood termites (Young, personal communication, 1967). Although in comparison with methyl bromide these mixtures do not have a deleterious effect on household materials, such as sponge rubber, they do not aerate after fumigation as rapidly as methyl bromide or sulphuryl fluoride.

Ruppel et al (1960) concluded that mixtures of acrylonitrile with carbon tetrachloride were not fully satisfactory against pests of stored maize in Colombia as compared with the EDC : CT 3 to 1 mixture commonly used in that country.

CARBON DISULPHIDE

In mixture with carbon tetrachloride, carbon disulphide (CS_2) is very useful for grain fumigation, especially in tall, upright silo storage units and in all storage units equipped with adequate recirculation systems. Enough carbon tetrachloride should he incorporated in the mixture to eliminate the fire hazard. A mixture commonly marketed for these purposes contains, by volume, 16.5 percent CS_2 82.5 percent carbon tetrachloride and 1.0 percent inert ingredients.

Another mixture useful for gravity distribution in concrete or metal grain bins contains 24 percent CS_2, 71 percent chloroform and 5 percent ethylene dibromide by volume.

CHLOROPICRIN

The highly insecticidal and lachrymatory properties of chloropicrin have been put to use by mixing this chemical with other materials for the fumigation of grain in farm or bulk storage units. It has been marketed in a mixture with methyl bromide or carbon tetrachloride (Cotton, 1963). A mixture of chloropicrin and methyl chloride 85 : 15 is recommended for forced distribution fumigation of grains (USDA, 1967).

ETHYLENE DIBROMIDE

Ethylene dibromide (EDB) is an ingredient of many important fumigant mixtures. As indicated in Chapter 6 it is highly insecticidal, and under normal conditions the residues remaining in foodstuffs are of a low order. These advantages are offset by the fact that EDB is considered to be very hazardous to mammals and is highly sorbed by materials undergoing fumigation. As a result, there may be poor penetration during actual treatment and prolonged persistence of the vapours in the fumigated commodity during the aeration process. Attempts to utilize the advantages and overcome the disadvantages have resulted in the formulation of a wide variety of mixtures. It is not possible to describe these in detail here. For the present purpose the subject may he discussed unifier two headings: liquid formulations and mixtures with methyl bromide.

LIQUID FORMULATIONS

Alone or with other toxic fumigants EDB is commonly mixed with carbon tetrachloride (CT) as a grain or local spot fumigant. The inclusion of CT as a high proportion of the formulation appears to add greatly to the effectiveness of EDB, principally because CT acts as an eluant for EDB in a column of grain and assists effectively in its downward migration (Berck, 1958). The following are some liquid formulations containing EDB in admixture with other materials (percent by volume) that have been widely used:

<u>Grain Fumigants</u>

EDB 5:	CT 95 – General grain fumigant
EDB 7:	Ethylene dichloride (EDC) 29: CT 64 – Gravity distribution grain fumigant
EDB 7:	Carbon disulphide (CS_2) 12: CT 81 Gravity distribution in flat storages
EDB 3.5:	EDC 10: CS_2 10: CT 76.5 – Gravity distribution in flat storages
EDB 5:	CS 24: Chloroform 71 – Gravity distribution grain fumigant

Local (spot) fumigants

EDB 20:	EDC 20: C! 60
EDB 59:	EDC 9: CI 32
FDB 15:	CT 85

ETHYLENE DIBROMIDE-METHYL BROMIDE MIXTURES

Mixtures of EDB with methyl bromide have been found useful for three main purposes:

- in the tropics to treat bagged plant products under gas-proof sheets;

- as local fumigants for treating food handling equipment in mills and food processing plants generally;

- as a fumigant for grain stored in bulk.

Bagged goods. In India, mixtures of the two fumigants in various proportions have been recommended for application under sheets or in chambers to treat different types of commodities in bags under warehouse conditions (Majumder, 1962). Treatment with the fumigant mixtures accompanied by simultaneous prophylactic applications of liquid insecticides to prevent reinfestation is known as the "Durofume" process (Majumder and Muthu, 1964). These authors give detailed recommendations for the proportions of the two chemicals required to achieve the best results with different materials.

A special applicator for administering fumigant mixtures of EDB and methyl bromide, which is particularly suitable for treating stacked commodities under gas-proof sheets, has been described by Majumder et al (1962). This consists of a brass or stainless steel tube held horizontally, containing the EDB. Above this there is a vertical scaffold into which a can of methyl bromide may be inserted. The methyl bromide can is pierced at the bottom by a probe, which connects to one end of the tube containing the EDB. The methyl bromide with its natural vapour pressure forces the EDB out through a discharge nozzle at the other end of the horizontal tube so that the mixture may be led through a distribution system above the stacked commodity.

Local fumigants. A mixture of seven parts of EDB and three parts of methyl bromide (weight to weight) has found wide use as a local or spot fumigant. This is best introduced by special applicators into holes bored at strategic points in the food handling equipment. This subject is dealt with in more detail in Chapter 8.

Bulk grain fumigation. The mixture has been found effective for bulk grain. The proportions of the two fumigants may vary according to the material being treated and the method of application. For cereal grain treatments the ratio of 70 : 30 EDB to methyl bromide is recommended for gravity distribution in smaller bins or farm

storages. For forced distribution systems, 30 : 70 EDB to methyl bromide is used. Majumder et al, (1963) found that the presence of methyl bromide improved the penetration and distribution of EDB in columns of grain and milled materials, the most effective proportions varying according to the material under treatment.

Dawson (1967) has taken out a United States patent for a yelled fumigant composition made by agitating different amounts of methyl bromide and ethylene dibromide in mixture with 3 to 5 percent by weight of colloidal silica. The gel thus produced retards the evaporation of the constituent fumigants and thus affords a convenient method for applying them to grain.

Insect toxicity. From the limited amount of laboratory evidence available to date, it appears that mixtures of these two fumigants are intrinsically more toxic to stored product insects than methyl bromide alone and at least equally as toxic as ethylene dibromide alone (Kazmaier and Fuller, 1959). These authors also concluded that the mixtures killed the postembryonic stages of Tribolium confusum more rapidly than either fumigant alone.

Penetration of flour. Heuser (1964) studied the pattern of diffusion through flour at 25°C of the two components of a 1 : 1 by weight mixture of EDB and methyl bromide. He found that the methyl bromide components in insecticidal concentrations could penetrate to 18 in (45 cm) after 48 hours, but EDB only penetrated effectively to 2 in (5 cm) after the same time. He concluded that if EDB is used "in high temperature zones to produce a longer lasting insecticidal effect in the surface layers than is obtained with M. B. (methyl bromide) for example where the gas proofing of fumigation sheeting is suspect, then its addition should be regarded as a supplement only, and not as in any Way replacing a proportion of the methyl bromide dose".

ETHYLENE DICHLORIDE

Compared with most modern fumigants, ethylene dichloride (EDC) is intrinsically not very toxic to insects but its mixture with CT, usually in the proportion by volume of 3 : 1 EDC to CT, has been used throughout the world as a successful fumigant for stored grain in a variety of structures. It has proved effective under tropical conditions in Africa (Hall, 1963). Its use for this purpose is contingent on a long exposure period, usually not less than 14 days, before the grain is turned or the fumigant aerated (Thompson, 1964). Such long exposure periods do not appear to have adverse effects on the grain. It may be applied either by gravity distribution or forced distribution systems.

This mixture has also been widely used as a seed fumigant. Properly used it does not have an adverse effect on the germination of seeds (Kamel and Shahba, 1958; Cotton, 1963; Parkin 1963).

METHYL BROMIDE-PHOSPHINE

A method for the combined use of methyl bromide and phosphine has been tested for treatments in oil-seed expeller, a dense material in which methyl bromide does not easily penetrate (Wohigemuth et al, 1976). The phosphine is found to diffuse into the expeller to give control while methyl bromide is effective on the outer surfaces. Furthermore, mixtures of methyl bromide and phosphine have been shown to have a joint action that improves the insecticidal effectiveness of both compounds (Bond, 1978; Bond and Morse, 1982; El Lakwah, 1978).

In this treatment, the phosphine-producing formulation is distributed evenly over the surface of the goods and, after sealing, the methyl bromide is applied through a tube by a double jet to vaporize in the Free space above the goods. Dosage of 56 g/m^3 methyl bromide and 4.4 g/m^3 phosphine at 29.5°C for 72 hours gave satisfactory control of Khapra beetle larvae.

METHYL CHLOROFORM

Methyl chloroform (1,1,1 - trichloromethane) has been tested under field conditions in mixtures with ethylene dichloride and the trials have shown that the two compounds interact physically to improve distribution of each component through grain bulks (UK, 1978). When applied with methyl chloroform, EDC is carried to a greater depth than when used alone, and the two compounds seem to act jointly to give a much enhanced toxic effect on insects. The physical properties of methyl chloroform relating to distribution and persistence compare favourably with carbon tetrachloride as does its toxicity to insects and mites. The available toxicological evidence suggests that it is a much safer compound than carbon tetrachloride for a pest control operator to use and tests on residues suggest that it should not be a toxic hazard in grain. The potential of methyl chloroform as a substitute for carbon tetrachloride in fumigant mixtures may be indicated by further testing in the future.

8. SPACE FUMIGATION AT ATMOSPHERIC PRESSURE

The term "space fumigation" is convenient for the designation of a wide range of treatments in enclosed spaces, which either contain infested materials or residual insect populations. The calculation of the dosage of fumigant to be applied is based primarily on the volume of the space. Other factors, such as the amount of a given commodity in the space, are sometimes introduced into the calculation for dosage. If facilities are available for the determination of fumigant concentrations at frequent intervals during exposure, it is advantageous to calculate the dosage on the basis of minimum concentration to be maintained in every part of the free air space during the required exposure time.

Fumigation may be successfully carried out in any structure that can be made sufficiently gas-tight for the length of time required. Infestations may often be dealt with on the spot without the necessity of moving the affected material.

SEALING METHODS AND MATERIALS

Since sealing techniques are common to all types of fumigation, these are outlined first. In practice, the choice of materials is largely influencer) by their availability.

NARROW CRACKS AND SMALL HOLES

Masking tape, heavy kraft paper applied with flour paste, caulking compound, paint-on adhesives, froth packs of Styrofoam, etc. may be used to cover or seal small cracks and holes. A vinyl plastic sealing compound is available that can be sprayed over all holes, cracks and crevices. This method, sometimes called "cocooning", is effective but requires a compressor for air, a spray gun and a hose. Instructions for carrying out the process are provided by manufacturers of the plastic; a full description is also given by Roop (1944). Webley and Harris (1979) describe the sealing and fumigation, using phosphine, of mud-brick stores in Mali.

LARGER CRACKS, CREVICES AND OPENINGS

Heavy kraft paper applied with flour paste and impregnated with a heavy grease or sheet of polyethylene sealed with masking tape may be used for larger openings. The vinyl sealing compound described above in the cocooning method can be applied to bridge larger openings and it will provide a relatively gas-impermeable, durable seal.

VENTILATORS OR OUTSIDE OPENINGS

Heavy kraft paper can sometimes be used but polyethylene sheeting is relatively inexpensive and can be re-used several times. It can be tied with ropes to make a tight seal around a ventilator.

FUMIGATION CHAMBERS

To conduct fumigations of commodities on a non-emergency basis, it is advisable to install a specially designed fumigation chamber. For many commodities the infestation may be controlled by fumigation at atmospheric pressure. Vacuum fumigation is recommended for the treatment of certain densely packed or absorbent materials. It is also used when a rapid turnover of certain goods is required. This technique is discussed in Chapter 9.

The purpose of a fumigation chamber is to allow fumigations to be carried out efficiently, safely and economically. The basic elements for design and construction should be incorporated in all chambers with variations made to suit individual needs. An effective fumigation chamber must be:

- soundly constructed so as to be gas tight;
- provided with an efficient system for applying and distributing the fumigant;
- provided with an efficient system for removing fumigant at the end of treatment;
- sited so as to handle infested goods conveniently;
- sited and operated so as to present no hazard to personnel working with or near the chamber (UK, 1973).

There is room for very wide variation in the design of atmospheric fumigation chambers. The fumigant to be used, the siting and size of the chamber, the type of goods and methods of handling, the availability of building materials, as well as the expenditure that can be allowed for increased efficiency and ease of operation, must all be taken into consideration. If chambers are used constantly or are loaded with heavy materials, a sturdy construction is necessary (Figure 22). However, light, portable chambers made from plywood or similar material may be appropriate for some types of treatment. A simple portable plywood chamber that was designed for travel from one forestry nursery to another is illustrated in Figure 23.

A portable gas-tight tent (shown in Figure 26) was devised by Brown and Heseltine (1964) and a full description of its construction and operation was given by these authors. It proved to be very useful for the fumigation of small commodity lots and for nursery stock.

STATIONARY CHAMBERS

Location

While the safest arrangement is to have the fumigation chamber located outside the main buildings, there may be circumstances in which it is safe to have it inside. If the chamber is properly constructed and equipped, it may be placed in a well-ventilated part of a building not regularly used by employees. When a chamber is located where

people are constantly working it may be separated from the working space by an additional wall with a ventilated space between.

The cost of loading and unloading the chamber largely determines the cost of fumigation. Therefore, by choosing 8 site which will permit the handling of goods in an efficient and economical manner, these costs can be reduced to a minimum. Some suggestions for locating a chamber in a warehouse are given in Figure 24.

After the removal of treated materials from a chamber, fumigants continue to diffuse. Therefore, the commodity must be kept on an open platform or in a well-ventilated room for 24 hours after treatment.

One important way to protect employees from exposure to fumigants is by means of a well designed exhaust system. This system should be equipped with one or more fans or blowers powerful enough to draw a continuous draught of air through the door into the outside atmosphere. A movement of air equivalent to one complete air change every one to three minutes in the empty chamber is recommended. If the chamber is located near dwelling houses, the exhaust pipe should terminate well above the roof of the building so that fumes may not enter occupied rooms during the aeration process. In some countries the spent fumigant is absorbed by passing the exhaust gases through absorbing solutions and degrading to harmless end products (Mori, 1980). For chambers up to 56 m^3 in capacity (2 000 ft^3), an exhaust stack reaching 4 m (13 ft) above the roof or any nearby structure should be adequate. When fumigants are thoroughly mixed with air, they dissipate rapidly on discharge into the open air from the fumigation chamber.

If the chamber is to be permanently fixed inside a building, it may incorporate a part of the floor, two existing walls and even the ceiling. A generalized plan indicating some of the essential features of an atmospheric fumigation chamber is shown in Figure 25. Suggestions for constructing a chamber from various materials, together with details of accessory equipment, are given below.

Size

The chamber size should be such that it can normally be loaded to its full capacity. There is, however, no difficulty in fumigating a partly filled chamber. While the dimensions of a fumigation chamber can only be decided by the owners, as a general guide a chamber should be approximately twice as long as it is wide with a height of 2-3 m. Even distribution of fumigant is more easily obtained in such a chamber than in a square one or one more than 3 m high.

FIGURE 24. - Possible positions for fumigation chamber in relation to storage facilities (UK, 1973)

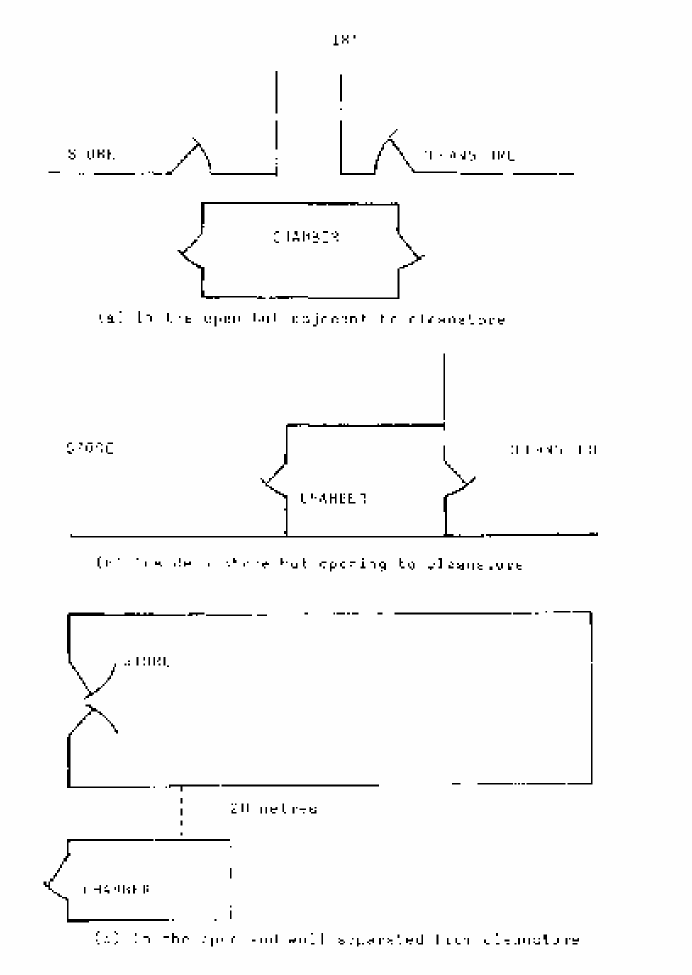
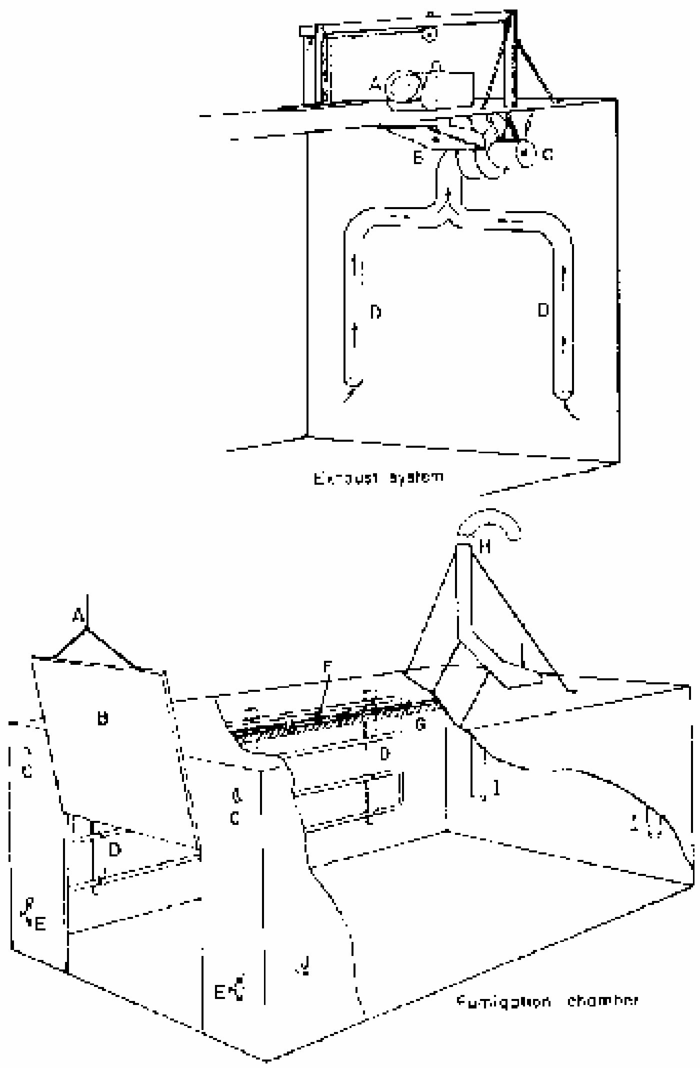


FIGURE 25 - Generalized plan of an atmospheric fumigation chamber.(J.E. King)



The maximum economic size is probably of the order of 100 m3. If a greater capacity is required, two or more smaller chambers often prove more economical and easy to handle. One chamber can be unloaded and reloaded while the second chamber is in use. The dimensions of the chamber are as important as the overall capacity, particularly where mechanical handling machinery is used. for instance, the size of pallets, if used, will dictate the proportions of the length and width. The height will depend on whether goods are loaded manually or with a fork lift truck (UK, 1973).

Construction Materials

The most satisfactory type of chamber, and one which is likely to give the minimum of trouble from leakage, is one with a concrete floor, walls of brick or poured dense concrete or other similar solid building materials and a flat roof of reinforced concrete. Chambers made of timber framing covered with sheets of material are likely to produce initial difficulties in sealing and continuing difficulties due to deterioration or

damage. When made of light materials, chambers are prone to leakage and may need an impermeable flexible film lining on the inner surface or regular renewal of the painted finish.

Paints should be applied, preferably by spraying, to give a continuous, impervious surface. A relatively durable finish can be obtained with an alkali-resisting primer followed by two coats of black oil paint and two coats of white. The use of the two colours facilitates inspection of damage after the chamber has been used (UK, 1973).

Construction

Walls. The outside walls of the chamber may be constructed wholly or in part of concrete, concrete blocks, sheet iron, plywood or tongue and groove boards. All these materials may also form part of the inner lining, but careful sealing of all joints and seams is essential.

Rough concrete and brick sorb fumigants and, if used, must be covered with hard finishing cement, with two or three layers of asphalt paint applied over its surface.

Plywood sheets, held by a framework of 5 x 10 cm (2 x 4 in) timbers, may be used for the interior walls of chambers.

All seams between sheets and at junctions of the floor with walls and ceiling must be carefully sealed with materials such asphalt cement or similar caulking compounds. With plywood it is advisable to seal all the inside surfaces with a primer, which is then covered with a suitable resin-base varnish. This protects the wood from moisture and reduces loss of fumigant through sorption by the wood.

If a plywood-lined chamber is to be subjected to rough usage with heavy bays or cartons, it is suggested that a sheet-metal lining be added. All joints and nail holes in the sheet metal should be carefully soldered.

When tongue and groove boards are used, they must be in two layers, placed diagonally, with a layer of roofing paper between. Insulation may be pieced between the layers if required. All joints must be sealed with great care, using a suitable cement. The inside surface should then be covered with a plastic film lining or with a primer and varnished as recommended above for plywood.

If a chamber detached from a building is to be used in the winter, it is recommended that the outer walls be of cement or brick. The inner wall may be made of plywood, which is separated from the outer wall by insulating material and a vapour barrier. Careful attention must be paid to the proper sealing of the plywood to prevent an accumulation of fumigant in the interspace.

Sheet or corrugated iron has been used successfully in warmer climates for the walls of chambers. When metal is used, great care must be taken to ensure proper sealing. All

seams and joints are liberally filled with mastic end the edges of the overlapping sheets covered with mastic tape. In chambers of this type, the ends, top end bottom of the corrugated iron well rest firmly in neoprene gaskets. It is necessary to have more support members than in a standard sheet iron building, in order to reduce expansion end contraction (Barnes and Reilly, 1956).

Ceiling. Lighter gauges of the materials recommended for the walls may be used for the ceiling. With plywood, a thickness of 1 cm (0.4 in) is usually sufficient. A detached permanent chamber must have a roof above the ceiling to provide all-year-round protection from the weather.

Floor. When the chamber is in constant use, and especially for treating bagged goods, a concrete floor is best. This should be reinforced to bear the greatest expected load. The concrete must be hard-finished to provide a gas proof, non-absorptive surface. Tongue and groove lumber or plywood, satisfactorily sealed as described above, may be used if built to withstand the loads. Plywood flooring of 1.2 cm (0.5 in) is often suitable for plants and nursery stock if it is well finished in the way described above.

Doors. The chamber can be provided with one or two doors, depending on its size and function. For larger chambers the use of two doors allows the loading of untreated material in one end of the chamber with unloading after treatment from the opposite end (Figure 24a and b). If a chamber is located inside a building, it may be built through a dividing wall with loading and unloading doors on opposite sides of the wall. The segregation of untreated and treated stock in this manner reduces the possibility of cross infestation.

The door should be as light as possible, it must give a gas-tight fit and it should be of good quality to withstand constant use. A stiff steel or timber frame clad with sheet metal on the inner surface may be satisfactory. The size of the door will be governed by the requirements for loading and unloading, but the smaller the door the easier it is to ensure a gas-tight fit.

Lift doors, which are raised above the chamber during loading and unloading, are very practical when a chamber is inside a building, because they are out of the way when open and do not interfere with the movement of the goods. Lift doors are operated by means of a counterweight and, if this works properly, opening and closing are easy.

Doors sliding on rails are better for installation on the outside of a building, where they can be rolled out of the way along an outside wall. An ordinary hinged door may be installed in a chamber if the materials to be treated can be moved in and out easily. Generally, the doors may be made of the same wood or metal materials, suitably finished, as recommended for the walls.

Door gasket. Proper closure is important because fumigants, such as methyl bromide, escape readily through improperly sealed doors. The best seal is provided by a continuous strip of rubber or neoprene that is soft enough to give a good seal but

resilient enough to recover well after continued pressure. Natural rubber may deteriorate after some time if used with methyl bromide, but is readily renewed. Overhead doors or hinged doors should fit neatly into flanges. The best seal is obtained with three strips of rubber, two on one surface, with a gap between that is just wide enough to receive the third gasket, which is on the opposite face. Sliding doors will carry only one strip of gasket on one surface, and this should therefore be 2.5 to 5 cm (1 to 2 in) wide. With all types of doors, particular care must be taken to make a gas-tight join between gasket strips, especially at the corners; this is best effected by liberal use of the adhesive material.

Door clamps. Door clamps are relied on to give a tight seal, and experience has shown that they should be placed not more than 30 cm (1 ft) apart all the way round the edge of the door.

For overhead and hinged-type doors, refrigerator door fasteners are recommended. Small, hinged doors not greater than 1.8 m (20 ft2) in area may be closed with ordinary sash fasteners 20 cm (8 in) apart. Sliding doors are forced against door frame gaskets by screw fasteners (Barnes and Reilly, 1956).

If the floor of the chamber is above the outside floor or ground level, the clamps may be extended all along the bottom. A sloping ramp is then required to load and unload the chamber. This may be drawn back when the door is closed. If the chamber floor is at outside level, it is not possible to clamp the bottom of the door unless special provision is made. A suggested arrangement is a shallow trench in the cement floor, which should be wide enough to allow sideways movements of the door and fasteners.

Circulation and venting. Proper circulation and postfumigation venting of the fumigant/air mixture are essential in atmospheric chambers. Efficient circulation ensures that the fumigant is rapidly and evenly dispersed throughout the chamber so that no part of the load is overdosed or under dosed, while forced ventilation removes the fumigant so that the chamber can be safely unloaded after the treatment. Circulation and forced ventilation are essential in large fumigation chambers and advisable even for small ones. A variety of fan systems can be used to achieve adequate circulation or ventilation and their size and capacity are governed by the volume of the chamber and the flow rate required. More details on types of fan systems are given by the U.K. Ministry of Agriculture, Fisheries and Food (UK,1973).

It is suggested that with most treatments of commodities the rate of air flow should give approximately one complete change of air every one to three minutes, based on the volume of the empty chamber. In selecting fans or blowers, due consideration must be given to friction in the exhaust pipe and other ducts in the system. Suppliers of equipment will provide the necessary specifications of the equipment required for a particular installation.

When non-flammable fumigants such as methyl bromide or ethylene dibromide are used, no protection from sparking is needed. With HCN, and other fumigants with wide

flammability limits, the motors of fans should be totally enclosed or, preferably, placed outside the chamber, with the blade shaft inserted in a gas-tight connexion in the wall.

The system should be designed so that the same fan will be used for circulation and venting. One method is to place the exhaust door, or port, near the fan so that when it is opened the fumigant/air mixture will be blown out into the open air. Another way is to use a blower with a large inlet and outlet. A diameter of 18 cm (7 in) is suitable. The outlet is fitted to a pipe of the same size. By means of a suitable blast gate or valve operated from outside, the air can be recirculated throughout the chamber by means of ducts or blown out through the exhaust stack into the open air.

If the ducts are used to draw the fumigant/air mixture from the bottom to the top of the chamber, distribution will be greatly improved from the beginning of the treatment. Ducts are best made from galvanized iron; the diameter required to give the suggested air flow of one complete change of air every one to three minutes will depend on the size of the chamber. A suggested arrangement is shown in Figure 25.

<u>Exhaust door or port</u>. The exhaust port may be a small door in the wall of the chamber; it should be at the opposite end of the chamber from the door so that after treatment, during venting and unloading, fresh air is drawn through the chamber from the open door. This exhaust port may slide open or move on hinges as a trapdoor. Experience has shown that the trapdoor may become a serious source of leakage. Great care must be taken to ensure that this door fits tightly in suitable gaskets and is firmly latched so that gas leakage is kept to a minimum. It is advisable to have the port in an accessible place so that it can be constantly checked.

<u>Heating and lighting systems</u>. A heating system is required if the chamber is used in cold weather. Sorption of fumigant on foodstuffs increases as the temperature decreases and, therefore, at lower temperatures larger amounts of fumigant are required and postfumigation ventilation is slower. As a general rule the temperature of the chamber and its load should be 15°C or above. If steam or hot water is available, it may be conducted through pipes set on opposite walls. A standard heating unit with blower may be used, which will also serve for fumigant circulation. However, such a blower should not be used for postfumigation venting unless the heat is turned off. Only non-flammable fumigants should be used in contact with steam pipes.

Electric or radiant heaters may be used if they provide adequate heat at short notice and if the elements are totally enclosed so that glowing wires may not come in contact with the fumigant. It is important to protect the heating units from mechanical damage and to protect the goods being fumigated from scorching or damage by the heater.

Lighting inside the chamber is often necessary since windows are usually omitted from fumigation chambers. The lights should be arranged so that the loading does not obscure them and they must be adequately protected against damage.

Application equipment. Gaseous-type fumigants are introduced from outside the chamber through tubing. Copper tubing is preferred for permanent installations, although a type of plastic tubing, which is not affected by the fumigant, may be used. The size and type of tubing will vary according to the fumigant used. Methods of application of important fumigants have already been given under separate headings in Chapter 6.

It is recommended that gaseous-type fumigants, such as HCN and methyl bromide propelled into the chamber under pressure, be discharged into a shallow galvanized iron evaporating pan, above 10 cm (4 in) wide and 5 cm (2 in) deep and two thirds the length of the chamber, which is suspended from the ceiling well above the load. This will speed evaporation and distribution, especially if the circulation fan blows downward above the surface of the liquid.

Liquid-type fumigants, such as ethylene dibromide, may be poured from a measuring cylinder into a small evaporating pan near the door. When non-flammable fumigants are used, they may be evaporated after the door is closed by warming the pan with a small, totally enclosed heater or heat lamp.

Accessories. There are several items of equipment that contribute to safety or help to achieve good results in the use of a fumigation chamber. All chambers that are not under constant surveillance during actual fumigation should be padlocked from outside. Also, a warning notice should be hung, or tacked, on the door while treatment is in progress. A small window or marine port (obtained from a marine hardware store) permits a view of the inside of the chamber so that thermometers or other instruments can be read from the outside.

One or more thermometers are essential for obtaining accurate readings of temperature in the free air space and in different parts of the load. The thermometers may be entirely inside the chamber or they may have gauges or dials on the outside with cables leading to the sensitive bulbs placed, as required, inside the chamber.

Sampling tubes for fumigant analysis, the number to be determined by the requirement to obtain samples of the gas from all representative parts of the space under fumigation, are useful accessories, which can aid in achieving efficient treatments. If they are installed at the time the chamber is built, they are available for use any time. The most practical arrangement is to have several copper connexions of about ().5 cm (0.25 in) outside diameter set at intervals at convenient points along one or more walls of the chamber. These are carefully sealed at both ends with removable caps or plugs. For sampling, the caps are removed and plastic or copper tubes leading to the gas analysis equipment are fitted to the outer ends of the desired sampling tubes.

When a chamber is inside a building, it is advisable to have a red electric light bulb over the door. This is turned on during the treatment to indicate that gas is inside the chamber. With fixed chambers, it is desirable to have an offset control panel on which

as many as possible of the recording instruments, electric switches, valve handles and other controls are situated. Such a unit simplifies operations and improves the appearance of the installation.

Pressure Leakage Test

Atmospheric chambers must retain the fumigant during the exposure period without appreciable loss through leakage to the surrounding atmosphere. The gas tightness of a chamber can be checked by a simple test where a positive air pressure is created and maintained in the chamber for a set length of time. An opening should be provided in the chamber to use a blower or other means to introduce air for creating the positive pressure. This pressure can be measured with an open-arm manometer filled with kerosene, which records the difference in kerosene levels in the two arms of the manometer. The time lapse for the chamber pressure to recede from 50 to 5 mm should be 22 seconds or longer. Inability to develop or maintain adequate pressure indicates considerable leakage and the chamber should be checked for leaks at seams, gaskets and other points. Repairs should be continued until the time for the pressure to recede is more than 22 seconds (for testing yes tightness of large structures see Chapter 11).

A smoke bomb or other device may be used in an effort to determine the areas of leakage (USDA, 1976).

Operation

Loading. The manner of loading the chamber will depend on the type of commodity and the method of handling it . A space of at least 30 cm (12 in) should be allowed between the top of the load and the ceiling. Goods can be stacked close to the side walls, provided they are not too near the heating units, but they should be kept clear of the end walls and at least 50 cm from the circulating fan. Bagged or packaged goods should not be placed directly on the floor. If these goods are not placed on platforms or pallets, a wooden floor rack with ample space between the slats should be provided. When methyl bromide is used, no extra space need be left between individual packages and bags because this fumigant penetrates well.

Temperature. The next step is to take the temperature of the material to be fumigated. Probe type "meat" thermometers have a pointed end and are suitable for placing in many materials. They are slow to respond, however, and sufficient time must be allowed for a correct reading. It is advisable to take temperatures in at least four well-separated points in the load. The temperature in the free air of the chamber should also be accurately determined.

For the purpose of selecting the appropriate dosage of fumigant, it is best to take the lowest temperature recorded, either in the commodity or the free space. As a general rule the temperature of the chamber and its load should be 15°C or above. Under certain circumstances, the fumigator should take into consideration the temperature at

which the material was kept for several days before the treatment, because this factor might influence the response of the insects during the fumigation. This point was discussed fully in Chapter 2.

Computing the dosage. The dosages for various fumigants and commodities are given in the Schedules. In some instances the concentration x time (c x t) products have been worked out and are given also; their use is dependent upon an accurate determination of concentrations present in the chamber throughout the treatment. Table 14 gives the ml per 100 ft^3 (2.83 m3), equivalent to certain dosages in terms of mg/l for a number of fumigants. For practical purposes, one mg/l is equivalent to one oz/ 1 000 ft^3 3.

Closure. When it is time to start the fumigation, the door is firmly clamped. (With liquids, discs or tablets this may be done after the fumigant is dispensed.) With most of the fumigants commonly used in chambers, the amounts introduced as dosage do not usually exert a significant positive pressure, especially when a full load sorbs some of the gas, or when there is a small amount of leakage. Therefore, all exhaust vents or ports must be tightly closed before the fumigant is introduced. If it is found in practice that considerable positive pressure is produced by the gas, one of the exhaust vents may be left slightly open while the fumigant is being introduced. If the fumigants that are used occupy a comparatively large part of the air space, 8 vent must be left open during application. Examples of such fumigants are the mixtures of ethylene oxide with carbon dioxide, and of ethylene dichloride with carbon tetrachloride.

Chambers used in the open may be equipped with small air pressure relief valves or exhaust tubes, which can be closed or capped as soon as application is finished.

APPLICATION OF FUMIGANT

The general manner in which each of the more important fumigants may be applied has already been described in Chapter 6.

Gaseous-type Fumigants

Fumigants, such as HCN and methyl bromide, are discharged from cylinders or other containers placed outside the chamber. When HCN is dispensed into an atmospheric chamber, it is necessary to apply additional pressure to the cylinder. This may be done with a tyre pump, in accordance with detailed instructions supplied by the manufacturer. When cylinders are used, they are placed on a platform scale and accurately weighed. The required dosage is then deducted from the total weight and the scale set at the lower point. The discharge valve on the cylinder is opened and closed quickly when the weight bar is again in balance.

Liquid-type Fumigants

Fumigants which are liquids at room temperatures are poured into a shallow tray or trough inside the chamber or are poured onto burlap sacks or similar material from

which they quickly evaporate. After the chamber door is closed, the circulating fans are started and the draught across the liquid or the sacked material hastens evaporation. As stated before, some fumigants with high boiling points, such as EDB, should be gently heated with a hot plate to hasten volatilization.

TABLE 14 - DOSAGE TABLE FOR FUMIGANTS USED IN SMALLER CHAMBERS

Quantities of liquid in millilitres per 100 cubic feet at 20°C equivalent to dosages in pounds per 1 000 cubic feet (to be used for measuring smaller quantities of liquids before evaporation in small chambers).

	LB/L 000 FT^3							
	0.0625	0.25	0.5	0.75	1	2	3	4
	MILLILITRES OF LIQUID/100 FT^3							
Acrylonitrile 34% + carbon tetrachloride 66%	2.1	8.5	17.0	25.6	34.1	68.2	102.3	136.4
Carbon disulphide	2.2	9.0	17.9	26.9	35.9	71.7	107.6	143.5
Carbon tetrachloride	1.8	7.1	14.2	21.3	28.4	56.8	85.2	113.6
Chloropicrin	1.7	6.9	13.7	20.6	27.4	54.9	82.3	109.7
Ethylene cholorobromide	1.7	6.7	13.4	20.1	26.8	53.6	80.5	107.3
Ethylene dibromide	1.3	5.2	10.4	15.6	20.8	43.7	62.6	87.4
Ethylene dichloride 75% + carbon tetrachloride 25%	2.1	8.4	16.9	25.3	33.8	67.5	101.3	135.1
Ethylene oxide at 7°C	3.2	12.7	25.5	38.2	51.0	102.0	153.0	204.0
Hydrogen cyanide	4.1	16.5	32.9	49.4	65.9	131.8	197.6	263.5
Methyl bromide* at 0°C	1.6	6.5	13.0	19.5	26.1	52.2	78.3	104.4
Propylene oxide	3.4	13.6	27.3	40.9	54.5	109.1	163.6	218.2

Conversion factors

100ft^3= 2.83m3- 11b = 16oz - loz/1 000 ft^3=g/m^3= mg/litre (approx).
1 fluid oz (Br) = 28.4 ml
1 fluid oz (U.S.) = 29.6 ml
1 ml = 0.035 fluid oz (Br)
1 ml = 0.034 fluid oz (U.S.)

* Methyl bromide is often dispensed as a liquid held under pressure in a graduated measuring glass, as a "280-ml applicator"

HCN Discs

If HCN discs are used in a chamber, they are scattered by the operator. In small chambers of up to 28 m^3 (1 000 ft^3) capacity, the discs can be scattered from the partly opened door. For this type of application, the fumigator must always wear a respirator.

Fan Circulation

After the fumigant is applied in the closed chamber, the circulating fans are operated for 15 to 30 minutes. With many commodity treatments, this initial circulation will suffice. When continuous or intermittent circulation is required, as for some fruit and plants, this is mentioned specifically in the fumigation schedules, which follow Chapter 15.

Exposure Time

The period of exposure to gaseous-type fumigants begins when the discharge of the fumigant is completed. With liquids and discs, the exposure should be timed from the moment the door is firmly closed.

The exposure periods for the various kinds of treatment at atmospheric pressure are given in the fumigation schedules. Fruit, vegetables, plants, bulbs and nursery stock are exposed usually for 1.5 to 4 hours; seeds and plant products, for 16 to 24 hours. For particularly sorptive commodities that may substantially deplete fumigant concentration, some allowance for this depletion may be necessary (see Thompson, 1970).

Venting and aeration

At the end of the treatment, venting should be commenced by opening the exhaust port or valve and starting the fan. The chamber door should be opened slightly to allow fresh air to flow in. At least 10 or 15 minutes should elapse before the door is fully opened. The time of this interval will depend on a number of factors, but the door should not be fully opened until the operator is assured by appropriate chemical tests, instrumental tests, or from long experience, that it is safe to enter the chamber to begin unloading. First aid kits and gas masks should be available and in good condition at all times.

MOBILE AND PORTABLE CHAMBERS

Fumigation chambers which can be readily moved from one place to another provide a flexible means of disinfestation. Such chambers, like the one illustrated in Figure 26, are often similar in construction and operation to stationary chambers, but of the lightest possible weight. The portable chambers shown in Figures 23 and 26 have

already been discussed. Two other types, making use of a convenient water seal for closure, are described below. These may only be used for fumigants such as methyl bromide and ethylene dibromide which are only slightly soluble in water. The actual surface of water exposed to the fumigant is small and does not affect the gas concentration significantly.

Portable Drum Fumigator

A small fumigation chamber (Figure 27), about 200 1 (7 ft^3) in volume, can be easily made from a clean steel or iron drum of the same size (50 gallons), as described by Johnson (1940). The best closure is a water seal arrangement with a lid fitting into a collar, or trough, built round the outside of the drum.

The head of the drum is cut out with a cold chisel and the rough edges smoothed. The collar is made of 20- to 24- gauge galvanized sheet metal and is tightly soldered or welded to the drum. The top of the collar should be about 2.5 cm (1 in) below the rim of the drum, so that if water is spilled it does not fall into the drum. A tap or plug near the bottom of the collar permits drainage.

The lid or cover is made of the same material as the collar. It consists of a disc and a rim, which fit neatly into the collar as illustrated in the figure. Disc and rim are carefully soldered or welded to provide a gas tight seam. One or two handles on the lid facilitate lifting.

A small fan or blower is necessary for the proper distribution of the fumigant. It may be operated by electricity from an ordinary lighting circuit or a battery, or manually by a hand-crank on the outside of the chamber with a chain drive connected to the blower axle. The manual arrangement is practical, as no reliance is placed on electric power. However, a special connexion must be fitted where the crank axle passes through the chamber wall. Heat may be provided by ordinary light bulbs, manually or thermostatically controlled. Fans and heating bulbs should be placed below the rack on which the load rests. This rack may be made of rat wire of 12 mm (0.5 in) mesh, or similar material.

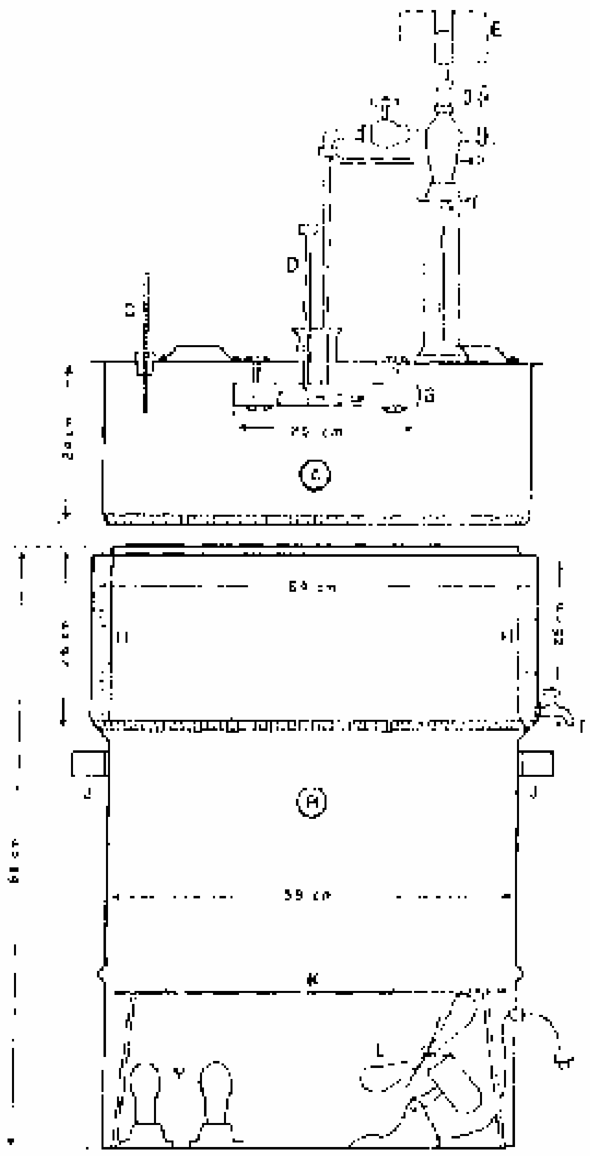
Where continuous circulation is required in a small chamber, a suitable small fan, with a high impedance motor, can be connected in series with electric light bulbs located on the outside of the chamber to serve as a rheostat. In this manner, the fan may be operated continuously during the fumigation periods with no increase in temperature because of the heat developed by the motor (Richardson and Roth, 1966).

Equipment such as dispensing tubes, plungers and thermometers may be inserted through gas tight fittings, for example rubber stoppers, in holes in the lid or sides. The water seal in the collar is satisfactory for fumigants such as methyl bromide or ethylene dibromide, which are only slightly soluble in water.

Methyl bromide may be dispensed from the 280 ml applicator already described, or from 20 ml ampoules which are placed in clips in a tray inside the lid before it is closed; the ampoules are thus broken by the plunger.

It should be pointed out that if an ampoule containing 20 ml of methyl bromide is released inside a drum of 200 l (approximately 50-gall) capacity, the resulting concentration will be about 170 mg/l (10.5 lb/1 000 ft^3 or 170 g/m^3). With this concentration, injury to growing plants may occur even if the exposure period is shortened to give an appropriate concentration x time (c x t) product. For plants, therefore, it is better to use the type of applicator illustrated in Figure 27 so that a small dosage may be applied.

FIGURE 27 - Portable drum fumigator for use with fumigants slightly soluble in water.



A. Lid
B. Drum
C. Thermometer
D. Plunger
F. 1-lb can CH3 Br
F. 28U-cc applicator
G. Evaporating pan
H. Water jacket
I. Drainage tap
J. Handle
K. Metal grille
L. Circulating fan
M. Heating lamps

If ethylene dibromide is used, the required amount is poured as a liquid into the evaporating pan. This can be done through a stopper after the lid is closed. Ethylene dibromide evaporates slowly and it should be heated with a small heating element without exposed wires, placed below the evaporating pan, in order that a full concentration of gas may be reached at the beginning of the treatment.

When the lid is placed in the water collar, it is necessary to release some of the air trapped inside the drum in order to allow the rim to be well below the water level and to prevent positive pressure being developed inside the drum. The air can be allowed to escape through one of the stoppers in the lid.

The drum should be painted on the inside with a primer and then given a resin based varnish or other finish appropriate to the fumigant principally used.

<u>Mobile Water-Sealed Fumigator</u>

The fumigator illustrated in Figure 28 is particularly suitable for use in large nurseries or similar establishments, where there is a fairly continuous flow of material requiring treatment.

The figure shows clearly the essential features of the fumigator. It has a water-seal to make a gas tight system and is designated primarily for use with methyl bromide for the treatment of nursery stock or rolls of turf which may harbour Japanese beetle larvae or other soil pests. With minor alterations to the design, other water-insoluble fumigants could be used. It is safe to use methyl bromide gas under an aluminium cover, but the liquid should never be left in contact with the metal for any length of time because of the possibility of fire.

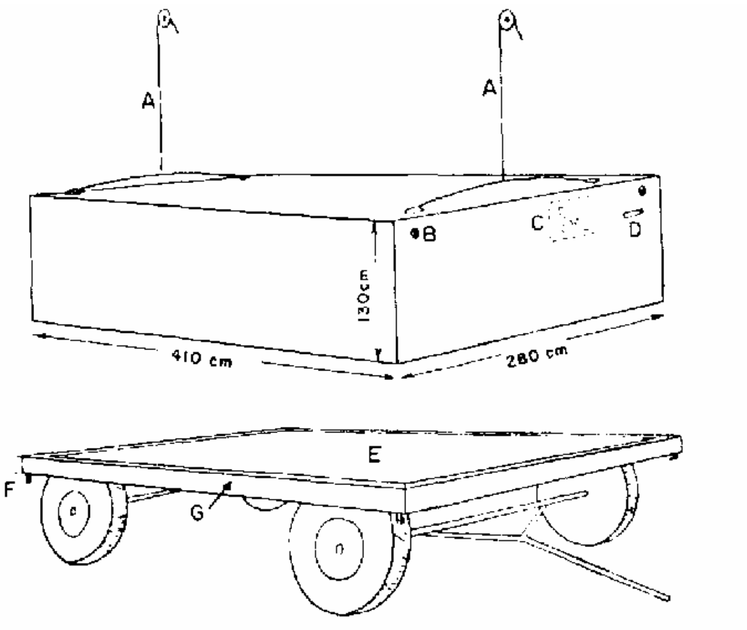
The air pressure release valve prevents the top section of the fumigator from being too buoyant and keeps it well seated in the water seal. Also, positive pressure created by the introduced fumigant may be released through this valve.

Mobile fumigation chambers that have facilities for applying and circulating the fumigant and employ gaskets to give gas tight seals are produced commercially. Models with capacities of 10 and 20 m are available.

Plain Steel Drums with Clamp-Type Lids

Where steel drums, equipped with removable, clamp-type covers and rubber gaskets, are available, they can be used as fumigation chambers without modification, except possibly for the holes required for the insertion of tubing and wire. The rubber gasket provides an adequate seal, but it should be checked occasionally for tightness.

FIGURE 28 - A water-seal fumigator with mobile base. Cover section fits inside trough when ready for fumigation



(Plant Pest Control Division, U.S. Department of Agriculture)
A. Cable attached to overhead pulley system to raise and lower cover section
B. Pressure relief valve
C. Internal electric fan
D. Connexion for fumigant applicator
E. Place for load
F. Water drainage point
G. IU-cm trough filled with water for sealing cover section

FUMIGATION UNDER SHEETS

Sheets retaining fumigant vapours for a sufficient time when placed over infested materials may provide a safe and effective method of fumigation. The word "tarpaulin" has in the past been used to describe these sheets, but this term is considered to be too general and may lead to a misunderstanding of the properties required for satisfactory treatments. Materials suitable for this type of work have been called "gas-proof sheets" (UK, 1974). This is a more descriptive term, although, in fact, all the materials so far used have been shown to differ somewhat in their permeability to fumigants (Phillips and Nelson, 1957).

This technique has widened the usefulness of fumigants by making it possible to treat infested materials without moving them from their place of storage or diverting them from their usual trade channels. Under some conditions it is possible to retain the sheets over the stacks of goods after fumigation and aeration, so that continuous protection is provided against reinfestation, contamination by bird droppings, water leaks, dust and dirt.

The information given in this manual should be sufficient to enable the operator to carry out simple small-scale treatments under a wide variety of conditions. If large-scale operations are contemplated, it would be advisable to consult the British bulletin (UK, 1974), which discusses the subject at some length. Particular attention should be given to details of piping and fumigant discharge suitable for large stacks.

MATERIALS FOR SHEETS

In recent years, the development of new plastic materials has led to the introduction of types of sheeting which are well suited for fumigation covers. The sheets used for particular jobs vary according to the amount of rough handling and the weather likely to be encountered. There have been several critical studies on the diffusion of methyl bromide (Phillips and Nelson, 1957; Waack et al, 1955) and phosphine (Wainman et al, 1975; Kashi et al, 1977) through various materials which might be used for fumigation sheets.

Sheets made of polyethylene or polyvinyl chloride film are suitable for use on the ground or to cover stacks in protected situations. The types most often used for fumigation have a thickness of 0.1 mm (0.004 in). Sheets of this gauge weigh less than 100 9 per m (2 lb per 100 ft2) and are easily handled even in large sizes. When sheets are to be used several times a thickness of 0.15 mm is recommended. Sheets made of these films tear easily on sharp corners or projections. They are not recommended for use on high buildings or structures when there is any possibility of high winds which may tear them to shreds. In some countries where the sheeting material is inexpensive and easily obtainable, it is often more economical in terms of labour to discard low density sheets instead of folding them up for further use.

For use in large-scale operations outdoors in exposed situations, coated fabrics are more suitable. Types that have been successfully used are nylon or terylene fabrics coated on troth sides with neoprene, polyvinyl chloride, or butyl rubber, and cotton fabrics, coated on both sides with neoprene.

Coated cotton fabrics appear to be more permeable to methyl bromide than the others. It has been found that a smooth slippery surface makes handling easier, especially if both sides of the fabric are coated (Brown, 1959).

Manufacturers of coated nylon fumigation sheets supply them with ropes sewn in plain hems on all four sides to facilitate clamping large covers together. For most fumigation purposes, the sheets are purchased in rectangular shapes. In certain circumstances, the overlapping of sheets is inconvenient and in such cases tailored covers may be more practical. For example, for the fumigation of large pyramids of groundnuts in northern Nigeria special covers tailored to the shape of the pyramids are used (Figures 29 and 30).

FUMIGATION OF STACKS

The goods most often fumigated under sheets are cereals and other plant products in bags. Cereals in cartons, dried fruit in boxes and tobacco in boxes or hogsheads can also be treated in this way. The fumigation of buildings under sheets is discussed in the following sections.

An important consideration in this type of treatment is the most efficient utilization of a sheet of a given area; the dimensions of the stack should be such as to provide the maximum volume. Appendix 1 contains a table of maximum volumes together with a formula for calculating them, based on data supplied by Bower (1961).

Today, the principal fumigants used for this work are methyl bromide and phosphine. Ethylene oxide and HCN have also been used, but HCN does not penetrate as well as methyl bromide (Redlinger, 1957c).

For further information on the use of fumigants for plant product fumigation under gas-proof sheets, the following references may be consulted:

Ethylene oxide-carbon dioxide mixture: Plant products generally, Thompson and Turtle (1953); snails in imported cargoes, Richardson and Roth (1963 and 1965).

Hydrogen cyanide (HCN): Plant products generally, Thompson and Turtle (1953); rice, Redlinger (1957c).

Methyl bromide: Plant products generally, Brown (1959); Hall (1963); Harada (1962); Hayward (1963); Puzzi et al, (1966); cotton seed, Hingorani and Kapoor (1964).

Phosphine (generated from aluminium or magnesium phosphide): Plant products generally, McGregor and Davidson (1966); Puzzi et al (1966); Esin (1967); rice in sacks, Gogburn and Tilton (1963); grain sorghum in sacks, Hubert (1962); maize, Lochner (1964a), flour in polythene-clad sacks, Wainman et al (1975), shrink-wrapped pallets of bagged cornmeal, Leesch and Highland (1978).

Ethylene dibromide-methyl bromide mixture: Majumder and Muthu (1964).

Dosages

Recommended dosages for this type of fumigation are given in Schedule P.

Preliminary Precautions

In addition to the usual precautions taken before any treatment, which have already been discussed, it is essential in fumigation under sheets that, after treatment, the gas escaping from the stack does not endanger any persons working or living in the vicinity. The fumigations may be conducted inside sheds, warehouses and similar structures, which furnish protection from bad weather (Figure 31). Such an arrangement is satisfactory if there is no possibility that gas may diffuse into occupied rooms or quarters. Very often the work can be safely done in warehouse rooms in which the windows can be kept open.

Suitable warning signs indicating type of fumigant and date of application should be placed on all stacks while fumigation is in progress, whether indoors or outdoors. First aid kits and gas masks should be readily available.

Preparation of Stack

A first step is to make certain that there will be no leakage of fumigant downwards during treatment. There is no serious loss or danger if the stack is placed on firm ground or on a good cement floor. If the floor is not gas proof, another gas-proof sheet, or even rolls of tar paper overlapped and sealed with masking tape, may be placed on the floor and the stack built above it.

When using methyl bromide or other similar fumigant it is essential that special provision be made to prevent the fumigant from discharging directly into sacks near the gas outlet. A suitable space may be provided by lifting and moving some bags from the top layer. In small piles, four bags may be propped against each other to form a "dome". Under this is laid a pan or can to receive the liquid discharging from the end of the outlet tube (see Figure 20). In larger stacks, a long space two bags deep and two bags wide should be made by lifting adjoining bags to form a trench. For these larger volumes, the outlets of the gas lines should be either spray nozzles, which ensure volatilization of the fumigant before the liquid reaches the bags or the sheeting, or open tubes leading into pans or cans in the manner already described.

If electrical power and outlets are available, one or more 25- or 30- cm (10or 12 in) fans, the number varying according to the size of the stack, aid greatly in distributing the fumigant.

Placing Sheets

Sheets of standard sizes are easily placed on rectangular or square stacks. It is preferable to have sheets large enough to cover the individual stacks. At least one foot of sheeting should be left on all sides of the stack to provide room for sealing the edges to the floor.

If the sheets are not large enough to cover the stack, one or more must be joined by rolling the edges together. According to Brown (1959), a satisfactory seal for methyl bromide fumigation may be obtained by rolling together about 1 m (3 ft) of the edges of each of the adjoining sheets. "The leading edge of the first sheet is folded back three feet. The second sheet is laid to overlap the first so that the edges lie together then these edges are held together and rolled until all the overlap is taken up. When covering a large stack, joins may have to be made in two directions." When sheets on stacks exposed to the wind or on buildings are joined, clamping of the rolled junctions is necessary. This technique is described in the following section, "Fumigation of buildings under sheets".

Under some conditions, such as those encountered in west Africa with the large pyramidal stacks, the rolling together of sheets is impracticable. Sealing with sprayed plastic has been tried with success but the standard practice is to use tailored covers for these stacks.

The edges of the sheets are best sealed to the floor by "snakes", plastic tubes about 10 cm (4 in) in diameter, filled with sand or water, which gives an efficient seal on level ground or floors. The use of water is very convenient because the tubes may be drained and rolled up between treatments. In emergency, some of the bags of the material already fumigated may be used, but a seal is difficult to obtain with these. Chains weighing not less than 2 kg per m (1.5 lb per ft) may also be used, but care must be taken that these do not damage the fabric. Outdoors, earth may be dug and piled closely around the base of the stack. Rips and holes appearing in the fabric may be repaired with adhesive or masking tape.

Applying Gaseous Fumigants

When gaseous fumigants, especially those containing methyl bromide, are applied indoors, respirators must be worn (see Figure 17).

For large piles the fumigant is applied from cylinders under pressure. With cylinders of methyl bromide discharging into high stacks, additional pressure in the cylinders may be needed before the full dosage is dispensed. For many treatments with methyl bromide, 1 lb cans are convenient (see Figure 17). The special applicator for

discharging the ethylene dibromide-methyl bromide mixture (Majumder et al, (1962) has been described in Chapter 7.

Acpiving Aluminium Phosphide

Tablets, pellets, sachets or other formulations used for generating phosphine may be applied to the stack before it is covered with the sheets. With long stacks it may be safer or more convenient to apply them as the sheeting work proceeds. It is often convenient to place paper trays containing the proportional number of tablets or pellets in strategic positions throughout the stack. The sachets are obtainable in lots of ten, bound together by string. These strings may be draped over the stacks in evenly spaced positions before the fumigation sheets are laid on.

Under normal circumstances, when the generation of the phosphine takes place slowly, it is not necessary to wear a respirator. When tablets, pellets or sachets are directly handled, rubber gloves should be worn. After the edges of sheets are secured with sand snakes, tape or other suitable material, warning signs should be placed on all sides of the stack. If the stacks are properly sealed, workers need not vacate the premises but good cross ventilation must be maintained during working hours and periodic tests with detector tubes or other suitable analyser should be made to ensure that no one is exposed to concentrations above the threshold limit value.

Fan Circulation

With gaseous fumigants, the fans should be operated for 15 minutes at the beginning of the treatment. Operation of the fans for a longer time will not greatly improve gas distribution and may tend to force the fumigant out, especially if the seal at the base of the sheets is poor.

Fan circulation is not recommended for phosphine treatments and should not be necessary if proper distribution is made of the aluminium phosphide before fumigation begins.

Leakage

When methyl bromide is being used, a careful check should be made with the leak detector around the entire base of the stack immediately after the fan is turned off. If the covering is made of more than one sheet, the rolled junctions should also be tested. Any serious leak can thus be found and corrected at once.

Aeration

During the process of airing, the operators must wear respirators while working on the stack or in its vicinity, until it is shown by an appropriate test that dangerous concentrations of the fumigant are not present. Aeration should be begun by quickly lifting several sheets of each corner of the stack. After an interval, more of the

sheeting may be lifted. When it has been demonstrated by the use of the leak detector, or by other chemical tests, that high concentrations of fumigant have diffused away, the sheets may be carefully drawn off the stack.

Special precautions, such as opening all doors and windows and running exhaust fans, should be taken when airing a stack indoors. Careful checks should be made to determine that the indoor space is safe for human occupancy.

Paper Coverings

A specialized method of stack fumigation is the use of kraft paper for covering dried fruit. This technique is an inexpensive and simple means of effective fumigation and subsequent storage. It is particularly useful on farms .

The enclosure is made by framing stacks of fruit boxes with 2.5 x 10 cm (1 x 4 in) timber and covering it with paper. The paper used by Barnes and Reilly (1956) consisted of two layers of heavy kraft paper with an asphalt laminant reinforced with sisal fibres.

The shape and construction of the stacks are important to success. They should be built on 10 x 10 cm (4 x 4 in) foundations to protect the fruit from ground moisture and to facilitate gas circulation. The frame is covered by carrying the paper up one side, across the top, and down the other side, allowance being made for 30 or 45 cm (12 or 18 in) widths for sealing on the ground. The paper strips are lapped about 8 cm (3 in) and then battened with laths. Since the cover papers shrink after weathering, allowance should be made for this by spacing the frame boards 2 m (about 7 ft) apart to take the edges of the 2.5 m (8 ft) wide paper. The paper cover is sealed to the ground with sand or fine soil. The seal should cover the paper on the ground completely and should be 15 to 20 cm (6 to 8 in) high against the sides of the structure. Head room above the boxes is necessary for gas circulation; if the stacks are not under a roof, they should be peaked to allow rainwater to run off. Tears in the paper may be repaired with masking tape.

After fumigation, several months' storage is provided by the enclosure, and reinfestation by insects is prevented. This technique, or modifications of it, could be applied to a number of similar storage problems.

FUMIGATION OF BUILDINGS UNDER SHEETS

Some buildings can be rendered gas tight only by the costly and time consuming sealing of individual cracks and holes, and it is often much easier to cover the entire structure with sheets (Figure 32). An early successful application of this technique was the commercial control of dry wood termites in dwellings. Formerly, thick kraft paper was laid over the buildings, but this material has been largely replaced by the modern types of plastic sheets already described.

The effectiveness of this method of insect control was demonstrated during the campaign to eradicate the Khapra beetle in California, in the course of which many large mills, grain elevators and warehouses were completely covered and fumigated with methyl bromide. In one of the treatments, the volume fumigated under covers was 113 000 cm (4 million ft^3) (Armitage, 1956). Rasmussen (1967) reported on a critical study of methyl bromide fumigation to control long-horn beetles in houses covered with gas-proof sheets during treatment.

The technique for fumigating large structures is basically the same as that already described for stack fumigation. There are a number of special requirements, however, brought about mainly by the fact that the covering sheets may be situated high above the ground and be exposed to winds of considerable velocity (Armitage, 1958).

Sheets. Although polyethylene sheeting may be used, the danger of its being torn by high winds, or even totally destroyed, has led to the use of the tougher, but much heavier, nylon or terylene fabrics coated with plastic. The weight of this material, best suited for covering buildings, varies between 200 and 440 g/m (6 and 13 oz/yd2).

FUMIGATION OF LARGE STRUCTURES

Recently, phosphine generated from aluminium phosphide has been successfully applied for the fumigation of large buildings, such as warehouses, which can be rendered sufficiently gas tight to retain the vapours. Special attention must be paid to the possibility of reaction with copper and copper alloys, as discussed in Chapter 6.

ADVANCE PRECAUTIONS

Preliminary Inspection and Arrangements

The structure to be fumigated should be carefully inspected at the outset so that unusual features or potential problems can be taken into consideration before the fumigation is started. Such matters as sources of leakage, commodities that will absorb large amounts of fumigant, possible damage to commodities, arrangements for gas analysis, safety of personnel, etc. should all be noted so that appropriate arrangements can be made beforehand. In preparation for fumigation, a check list of the various duties to be performed should be made - a fumigator should never trust to memory or assume that essential things have been done. It is important to instruct the fumigation crew carefully, show them any special problems or hazards and inform them of emergency procedures in case of an accident.

Compliance with Official Regulations

The use of fumigants is often regulated by local or state governments. Regulations are designed to protect the health of those applying the chemicals and of the public in general. Regardless of whether the treatments are made regularly in permanent

installations or are carried out once only in a particular place, it is necessary that all regulations be observed.

Advance Notice of Treatments

It is usually advisable to inform local fire departments of large-scale treatments, especially if an entire structure or building is to be fumigated. The police should also be warned if the work is being done in a built-up area.

Guards

If the fumigation is being done in a place accessible to the public or adjoining public thoroughfares, it is necessary to employ one or more guards to keep unauthorized persons from approaching the fumigation site or from interfering with the operation. The guards are employed to keep outsiders away while the fumigation is being prepared, during the gas application, during the treatment and until the entire fumigation area has been declared "gas free" after the treatment has ended.

Warning Notices

Regardless of whether guards are employed or not, properly worded warning signs should be posted on all sides of a fumigation site. These signs should have clearly printed letters at least 5 cm (2 in) high, with wording such as:

DANGER
FUMIGATION WITH POISON GAS
(name of particular fumigant)
KEEP OUT
BY ORDER

The date of application of the fumigant should be included on the warning notices for those treatments where there is a possibility that the notices may not be removed at the end of the fumigation, e.g. on freight containers, railway box cars or other transportation vehicles. Notices printed on cardboard are often available from the fumigant manufacturer or dealer.

Respirators

Fresh, unused respirator canisters, specifically designed for protection against the particular fumigant to be employed, should be provided for each operator likely to be exposed to any concentration of the gas. A minimum number is two canisters per operator. One is to be used during application of the fumigant and, if there is exposure to any fumigant during this operation, it should be replaced by a new one before the aeration process begins.

Careful checks of individual respirators, carried out under the supervision of the foreman or leader, should be made by all operators concerned. All precautions and procedures outlined in Chapter 3 (Respirators) should be carefully followed.

PREPARATIONS FOR FUMIGATION

Sealing

Particular attention must be given to the proper sealing of a structure, as this may constitute the difference between the success and failure of a fumigation. Brick or cement buildings in a good state of repair can usually be fumigated by sealing all external openings by any of the methods listed at the beginning of this chapter. Doors and windows should be firmly closed and almost invariably should be taped or caulked. If the entire building cannot be made gas tight, it may be covered with gas-proof sheets in the manner described in the previous section.

Circulating Fans

When methyl bromide is being used, artificial circulation should be provided by means of fans to prevent stratification of this heavy gas and to ensure even distribution. One 40 cm (16 in) fan is usually sufficient for every 1 400 m^3 (50 000 ft^3). Provision should be made to switch the fans on or off from outside the building.

Plan for Gas Discharge

All fumigations which are not strictly routine in nature must be carefully planned. If a particular operation is complicated or conducted on a large scale, it is well to have the duties and movements of each employee typed out on a specially drawn-up work sheet. When fumigating buildings, warehouses or ships with more than one floor or deck, it is advisable to include a plan on this sheet showing the location of each fumigant cylinder and gas outlet and all exits and entrances. When crews are fumigating large structures by releasing the fumigant from inside, it is sometimes advisable to place directional signs at strategic stairways, doors or turnings. Sometimes it is helpful to chalk arrows and other marks on the floor to indicate the direction and order of movements.

The work should be organized so that at no time will the operators pass through a room or space in which the gas has already been discharged. In buildings without basements, discharge should start on the top floor in order that the crew may work toward the prearranged exit on the ground floor. If there is a basement or cellar, a special plan may have to be made. Usually, the main floor may be omitted while one crew releases the fumigant in the upper floors and another works in the basement. The main floor is not treated until the others have been traversed and all operators, except those concerned with the final discharge, have left the building.

It is most important that operators should not be releasing fumigants inside a building for more than 30 minutes. It is better that a 15- to 20- minute period be allowed for each person. If the gas release cannot be done properly within that time by the available staff, more workers should be allocated to the crew during the preliminary planning.

In large operations, it is good practice to have the crew working in pairs; if an accident occurs to one person, the other can bring him into the fresh air or summon assistance. Each member should be fully acquainted with the role of the others in the team. When the discharge of the fumigant is to be done by operators moving inside the structure, a full rehearsal of the procedure should be carried out at least once before the actual fumigation is started.

Calculation of Dosage

All dosage recommendations are made on the basis of the volume (cubic content) of the structure. For regularly shaped square or rectangular buildings, dosages are calculated by multiplying length by width by height. If the buildings are irregular, the volume of each unit should be calculated separately, and then all added together. If the building has a peaked roof, the average between the height of the sidewall and the distance from the lowest floor to the top of the roof may be taken as the height dimension (third multiple) in calculating the volume of the structure.

No allowance should be made for space occupied by commodities, materials, machinery or furnishings. Dosage recommendations are given in Schedules P and Q.

Provision for Ventilation

If possible, some provision should be made in advance for starting postfumigation ventilation before the fumigators enter the buildings. If front and rear doors can be opened from the outside, a strong draught can be created to dilute the gas concentrations appreciably when ventilation is started.

When the roof ventilators are covered with plastic sheeting or kraft paper, they can be quickly and safely uncovered at ventilation time and the fans can be started.

Final Checks

When all preparations are completed, several checks should be made before the fumigants are applied.

1. Sources of ignition. All possible sources of fire should be eliminated. All pilot lights and gas and oil burners should be extinguished. It is particularly important that thermostatically controlled, high temperature electrical equipment of any kind be disconnected during the fumigation. HCN is inflammable at the high concentrations that may be present during initial discharge of the gas. Methyl bromide may react in

the presence of a flame or glowing wire to form hydrobromic acid, which may be corrosive or injurious to many materials.

2. Warning signs. Ascertain that the warning signs are properly placed on all possible entrances to the building, and, in large-scale operations, at strategic points on the approaches to the building.

3. Outside telephone. Locate a nearby telephone of ready and constant access which may be used in case of emergency.

4. Guards. See that the guards or watchmen are at their proper stations before gas discharge begins. They should prevent unauthorized persons from entering the building or interfering with the work of the fumigation crew.

5. Check on evacuation. As a final essential measure, the foreman fumigator, accompanied if necessary by senior crew members, should visit every floor and room of the structure calling in a loud voice a warning, such as: "Poison gas fumigation to begin everybody out." Failure to observe this precaution in the past has led to serious accidents, including at least one fatality. During the visit these operators will also have an opportunity to see if all other preparations are properly completed.

APPLICATION OF THE FUMIGANT

While the fumigant is being applied, all persons engaged in or associated with this operation should wear respirators (gas masks). The only permissible exception to this rule concerns the operators working in the open, or in some well-ventilated place, under conditions in which any gas that escapes from the equipment is immediately diluted and dissipated. The respirators should not be removed until the workers indoors have reached fresh air, the fumigant has been completely discharged, and all the valves and piping have been closed so that no fumigant can escape from the system.

During the application, unauthorised persons should not be allowed to approach or talk to the operators engaged in the discharge of the fumigant. The organization of fumigant discharge was also discussed earlier under "Plan for gas discharge". Special techniques for HCN and methyl bromide are given later in this chapter under the headings for each gas.

PRECAUTIONS DURING TREATMENT

During the course of the treatment regular checks should be made for leakage of the fumigant. This is necessary for safety and also to prevent a failure of the treatment. The sections dealing with the properties and uses of fumigants include descriptions of methods of leak detection.

When guards are posted during large-scale operations they should be on duty during the whole period of treatment.

FUMIGANT ANALYSIS

As an aid to effective fumigation, sampling tubes should be connected to strategic points throughout the structure. During the fumigation, samples may be drawn at intervals and analysed by one of the methods already described for the fumigant being used. If concentrations at any point fall below an established level, more fumigant may be introduced as required.

VENTILATION

The operators should wear respirators when they approach or enter the building.

Openings from Outside

In accordance with preparations made before fumigation, when airing begins, as many doors and windows as possible are opened from the outside. Ventilators and fans with readily accessible switches may be started. The operators should then withdraw from the immediate vicinity of the fumigated structure. At least 30 minutes should elapse before the fumigators enter the building to open more doors and windows and to start other ventilators. At the beginning of aeration, the building should be entered only for short periods of time. The process of ventilation may be divided into stages, with ample time given to each one. After being in the building for a short period, the operators should withdraw into fresh air, remove their respirators, and wait for 15 minutes or more before putting them on again and re-entering the structure.

Tests for Gas-free Condition

As soon as the crew foreman determines that the structure is properly aired, the appropriate chemical tests for residual fumigant, already described, may be carried out.

Particular attention should be paid to the retention of gas in highly sorptive material such as flours, meals and jute bags. This retention may be unduly prolonged by introducing cold air into a building that was warm during the fumigation. Serious accidents may result from closing such a building again and warming it up and causing the release of sorbed gas into the atmosphere. In cold weather, therefore, after the preliminary aeration, all doors and windows should be closed, the building heated to above 24°C for two or three hours, and the aeration repeated. Under exceptional conditions, this process may have to be repeated two or three times before all material is safely free of gas.

After chemical tests have shown that both the structure and its contents are free from toxic concentrations, the building may be declared gas free and reoccupation permitted.

APPLICATION OF HCN

The materials from which HCN may be volatilized as a fumigant were listed in Chapter 6. The techniques for their practical application in building fumigation are described here.

Pot Method

The generation of HCN by the action of sulphuric acid on a cyanide salt is usually referred to as the pot method, although wooden barrels are often used as well as crocks or pots. This is not as convenient as the other two methods described below, which have largely replaced it, but it lends itself to emergency treatments.

Handling Chemicals

Sulphuric acid, 66° Beaume, is usually supplied in 45 1 (10 gall) carboys in wooden frames. It is advisable to divide this into smaller amounts in bottles; for this operation, a tilting frame is recommended. Acid should be poured slowly and with caution.

The sodium cyanide eggs, usually 25 9 (l oz) each, should be kept in tightly closed containers, away from heat and moisture, until they are needed.

Precautions

Sodium cyanide is a powerful stomach poison, which can also cause serious poisoning by being absorbed through cuts and exposed skin. **All persons handling the dry sodium cyanide, and mixing the sulphuric acid in water before fumigation begins, should wear rubber gloves and tight fitting goggles.**

CHEMICALS ARE MADE READY IN THE FOLLOWING PROPORTIONS ACCORDING TO THE SYSTEMS OF MEASUREMENT USED.

	METRIC	BRITISH	U.S.
SODIUM CYANIDE	1.0 kg	1.0 lb	1.0 lb
SULPHURIC ACID	1.5 litres	1.2 pints	1.5 pints
WATER	3.0 litres	2.4 pints	3.0 pints

(Actually, it has been shown by chemical test that a 1 : 1.5 : 2 United States formula yields more gas than the one given. However, it has been observed that the smaller

quantity of water used may result in a crystallization of the residue, which makes the emptying of the containers after fumigation more difficult (Back and Cotton, 1942).

Dosage

If properly generated according to the method given here, O.45 kg (1 lb) of sodium cyanide will generate 0.25 kg (8 oz approximately) of HCN gas. For many building fumigations at temperatures above 20°C, the dosage of HCN gas recommended is 8 g/m^3 (8oz/l 000 ft^3).

Use and Placing of Generators

Earthenware crocks up to 18 1 (4 gall) capacity or clean, water-tight 227 l (50 gall) wooden barrels should be used as generators. For large-scale operations in mills and warehouses, the barrels are safer to use. The generators may be set out in groups of three or four on each floor of the building, each in a galvanized iron washtub, if available. The tub should contain a pailful of water with several handfuls of washing soda to neutralize any acid that may leak or spill from the barrel. The generators may be conspicuously numbered in the order of their use, in accordance with the need for careful planning discussed previously.

Preparing for Generation

After the generators are set out in their final positions, the required amount of water is poured into each. Then the required amount of acid for each generator is measured into pails. Next, the acid is poured carefully and slowly into the water in the generators.

Caution: never, under any circumstances, pour water into sulphuric acid - always acid into water

The next step is to count the number of sodium eggs required for each generator and to place them in double-walled kraft paper bags or flour sacks. The bags or sacks are then carefully placed 30 or 60 cm (1 or 2 ft) away from the generator, where they can be easily seen and reached.

Generating the Fumigant

After the final preparation and inspection of the buildings have been made, the respirators, fitted with anticyanide canisters, are put on. Gas generation is started at the farthest point from the final exit (see previous sections for discussion of planning). As each generator is reached, the operator carefully lowers the bag with cyanide into the acid, without allowing any liquid to splash on his person. Then he moves quickly to the next generator and repeats the same procedure at each station until he reaches the final exit.

Cleaning Generators

After the fumigation is finished and the structure has been thoroughly ventilated, the residue must be emptied and the generators cleaned. Sometimes the chemical reaction is incomplete and therefore it is advisable to wear a respirator while handling the generators and emptying them. The residual material should be taken to properly approved sites for disposal. The empty generators should then be thoroughly washed with fresh water and the liquid disposed of in the manner already suggested.

Special Pressure Generators

Special generators made of acid-resistant metals are available from some manufacturers of sodium cyanide. They permit the generating of HCN outside a structure. The acid is placed at the bottom of the metal generator and the sodium cyanide, preferably in egg-shaped form, is suspended above in a metal basket. The lid of the generator is then tightly clamped down with thumbscrews. When the charge of HCN is to be released, the basket of sodium cyanide eggs is plunged into the acid and the generated gas flows through a rubber hose into the fumigation space. This method is especially suitable for releasing HCN into fixed installations.

Liquid HCN

If liquid HCN is available in steel cylinders, this is one of the most convenient ways of applying it on a large scale. This method is commonly used in countries where HCN is manufactured, or where it may readily be shipped. (Note that a time limit is set for the return of cylinders see Chapter 6).

The cylinders are always discharged from the outside of the structures being fumigated. This feature adds to the convenience and safety of the method. For fumigation of buildings and ships, the HCN must be forced under pressure through piping. For this purpose, air compressors are connected to a special valve on the head of the cylinder to drive the liquid through a siphon tube out of the discharge valve into the lines (see Figure 20).

Some premises, which are regularly fumigated with HCN, have a permanent piping system of copper tubes and the necessary connexions. When buildings are fumigated occasionally, a temporary piping system made of rubber hose is used.

The manufacturers and suppliers of liquid HCN in cylinders supply comprehensive and detailed manuals covering all aspects of its application, together with full instructions for the installation of piping systems.

Absorbed HCN

The use of HCN absorbed in porous materials such as cardboard discs, which has already been described, is a convenient method of dispensing the gas. The

hermetically sealed cans hold a standard amount of HCN, usually 0.5 or 1 kg (1 or 2.25 lb) approximately. Some brands are available with small amounts of added warning agents, such as chloropicrin.

The use of HCN discs must be carefully planned according to the system already described.

Cooling. The discs should be precooled for several hours before treatment begins. This can be done by immersing the cans in tubs of water containing ice, by placing them in a refrigerator overnight, or by surrounding them with dry ice. The use of dry ice is especially suitable during hot weather.

Protection of floors. To prevent floors or floor coverings from being marred, the discs may be emptied onto sheets of corrugated or ordinary wrapping paper of about 1 m^2 (1 yd).

Opening cans. The cans are quickly opened with the special can opener, as illustrated in Figure 21. **Respirators must always be worn when cans of discs are opened or distributed.**

Distributing cans. In the fumigation of large buildings with two or more floors or many rooms, it is advisable to open the cans at the points of distribution and immediately cap them with the fibre caps that act as protection for the cans during shipment. When fumigation is started, this provision enables the operator to empty the cans and scatter the discs.

Scattering the discs. The fumigating crew of not less than two men should work according to a prearranged plan and proceed toward the final exit in the manner already described.

In hot weather, HCN evolves rapidly from the discs and the operators may have to move quickly to avoid working in poisonous atmospheres.

Disposing of discs. Under normal conditions, the used discs are free of HCN by the time the structure is opened for ventilation. Nevertheless, all discs should be carefully gathered and burned in the open, or taken to an approved disposal site.

APPLYING METHYL BROMIDE

Liquid methyl bromide should not come directly in contact with painted surfaces. This can be avoided by volatilizing the spray in the free air or by discharging the liquid into metal pans or cons with a large surface area.

The fans provided for methyl bromide fumigation should be operated for 15 to JO minutes at the beginning of a fumigation. Once equal distribution has been attained, the gas/air mixture remains in equilibrium almost indefinitely and the methyl bromide

does not stratify during the period of fumigation. However, if gas analysis at any time indicates unequal distribution, or any additional fumigant is discharged during treatment, the fans should he operated again for as long as is considered necessary.

Direct Discharge from Cylinders

Methyl bromide cylinders may be placed, according to dosage requirements at strategic points throughout the structure so that the valves may be fully opened by the operators, wearing respirators, as they retreat toward the final exit.

In large operations, or in structures with high ceilings or roofs, stand pipes (curved copper tubing directed upward) are often attached to the cylinder outlets. In this technique, a short "T" is fitted to the top of the pipe to discharge the gas laterally and prevent contact with the ceiling.

Hot Gas Method

Methyl bromide may be discharged from outside the building by passing it through a heat exchanger after it leaves the cylinder. This is the method already described for the fumigation of buildings under tarpaulins.

Recirculation Method

Another method, applicable in low structures that are not covered by tarpaulins, is the use of plastic ducts similar to those used in the fumigation of grain by the recirculation technique. To prevent the collapse of plastic ducts at bends, short metal ducts of the same diameter are introduced into the line wherever it is necessary to change direction. A fan draws air from the ground floor and forces it through the duct back into the building through an upstairs window. Methyl bromide is introduced through tubing on the intake side of the fan and is thus distributed throughout the building.

Pressure Method

For discharging methyl bromide into flour mills or other tall buildings from the outside, the fumigant may he forced through the lines by compressed air. The liquid flows through flexible copper tubing of 9 or 12 mm (0.375 or 0.5 in) outside diameter. At the outlet end, each tube is pinched to give an aperture of 2 mm (0.08 in) width. The outlets are directed laterally or upward, but never downward. Some manufacturers add nitrogen or another inert gas above the liquid in the cylinder in order to supplement the natural vapour pressure of the fumigant. This combination is usually sufficient to start the methyl bromide through the lines, even in tall buildings. When the cylinder is half empty, additional pressure up to 10.5 kg/cm^2(50 lb/in2) may be provided from a compressor in order to complete the discharge.

APPLYING PHOSPHINE

A number of formulations for generating phosphine are available for the fumigation of large structures. When tablets or pellets of aluminium phosphide are used, they are distributed on trays or thick paper at intervals throughout the building. Similarly, magnesium phosphide plates are laid out to give an even dispersion of the required dosage. If there are one or more storeys, the operators start at the top floor and work downward toward the final exit. As suggested in Chapter 6, under normal conditions evolution of the phosphine is delayed and it is not necessary to wear respirators if the distribution can be completed in a few minutes. If there is a possibility of considerable delay, or under conditions of high temperature and humidity, respirators should be worn at the discretion of the official supervising the fumigation.

For small structures, where the work can be completed in a few minutes, sachets may be employed by suspending them evenly on thin rope as from a washing line.

At the completion of the fumigation and aeration, the residual powder from the tablets or pellets or the used plates or sachets must be carefully collected and safely disposed of, as described in Chapter 6.

MILL FUMIGATION

Methyl bromide and phosphine are effective in the fumigation of modern concrete, stone or brick mills that can be made sufficiently gas tight to retain the fumigant. HCN may be satisfactory for mills which allow more leakage, such as ones with frame or sheet metal construction. number of special measures must be carried out when mills are fumigated in order that the fumigant may penetrate all parts of the machinery and equipment. These are especially important with HCN because it does not penetrate well into accumulations of flour, meal or other sorptive materials.

PREPARATIONS FOR HCN FUMIGATION

The following is a summary of the more important measures to he taken (Cotton, 1958):

1. Before stopping the mill. Shut off the source of grain fed to the mill. Then continue to run the machinery until 811 parts of the milling system are empty. At the same time, remove elevator boot slides so that stock may be pulled out and not carried forward. Use a rubber mallet or a similar device that will not damage the equipment to hammer all parts of the machinery from which accumulations of flour, meal or dust can be dislodged.

2. After stopping the mill. All machines, ducts, bins and conveyors in the entire mill should be thoroughly cleaned. All infested material collected in cleaning the mill should be removed to the fumigation chamber and fumigated or the debris should be taken outdoors and buried. All doors to conveyor boxes and bins, and those leading to

enclosed machinery, should be opened as widely as possible to aid gas penetration. It is especially important to open the "dead" spouts into which the fumigant penetrates with difficulty.

3. Machinery piping system. Fumigation of the various units of the mill and its machinery is assisted by the installation of a special piping system equipped with nozzles which automatically deliver equal quantities of fumigant to each unit. An installation of this type leads to a considerable saving of fumigant. Also, it may eliminate the necessity of dismantling and cleaning the machinery, and labour costs may thus be greatly reduced. The manufacturers of liquid HCN supply information on the planning and installation of such systems.

PREPARATIONS FOR METHYL BROMIDE AND PHOSPHINE FUMIGATION

These two fumigants penetrate well into accumulations of sorptive mill products and trash lying in a mill. Therefore, if methyl bromide is used, the cleaning programme required before HCN fumigation can be delayed until after the fumigation is completed. In fact, this is recommended because the insects are killed where they are and the debris does not need to be moved to a special fumigation chamber.

All doors or vents to bins, conveyors and machinery should be opened as already outlined for HCN fumigation. Further information on the biology and control of insects in flour mills is given by Hill (1978).

LOCAL FUMIGATION

Local fumigation is the treatment of isolated insect infestations in buildings. In mills, the term is applied particularly to the fumigation of individual machines and enclosed equipment that harbour insects. The popular term "spot fumigation" applies to this type of treatment as well as to treatments of isolated outbreaks in stored grain, which are discussed in Chapter 10.

The fumigants used for this work are pure compounds or mixtures that evaporate slowly and do not diffuse quickly from the treated locality into the main space of the building. Some of the more common formulations are given in Schedule R and in Chapter 7. Although these vapours diffuse slowly, they kill insects only when the equipment is fairly tightly enclosed. It is usual to apply the fumigants during weekends or at night after the mill has been shut down. They should be applied regularly every two or three weeks. A regular programme of local fumigations may keep insect populations at a low level throughout the year. This contributes to the production of goods free from infestation. However, only in exceptional circumstances does such a program eliminate the need for occasional general fumigations. Local fumigation may be done by alert and competent mill employees who are assigned to this work and specially trained for it. (See also White et al, 1957; Cotton, 1961, 1963; Hill and Armstrong, 1952; Hill, 1978.)

PREPARATIONS

Before local fumigants are applied, the mill should be run dry. The milling stock should not be removed until after treatment. All vents from milling machinery to the outside should be closed and other steps taken to reduce draughts in the mill system as much as possible. Dead spouts and filled suction lines should be cleaned.

PRECAUTION

In all applications of local fumigants, the operators should wear industrial type respirators fitted with the proper canisters. Care should be taken not to spill liquids on skin or clothing.

METHODS OF APPLICATION

There are two principal methods for the application of local fumigants in mills: hand application and injection by automatic applicators.

Hand Application

When the fumigants are applied by hand, the dosages for each locality may be poured from the shipping drums into litre or quart bottles, which are then placed individually beside each particular point of application. It is best to use bottles graduated in millilitres or fluid ounces so that the correct dosage may be applied at each station. The operators should work in pairs.

With hand applications, the usual procedure is to start at the top of the building and work quickly downward from floor to floor as the liquids are poured or dashed into the individual units. After each application, the opening is tightly closed. The empty bottles may be abandoned and picked up when the building is finally aerated after fumigation. Windows should be left open during application but closed on each floor as the team works downward.

When application is completed, all doors or other entrances should be closed and locked. Warning signs should be posted at all possible entrances and a guard placed on duty; these and other precautions should be generally the same as for all building fumigations.

If possible, the mill should not be opened until 24 hours have elapsed from the time of application. If only one night i allowed for treatment, exposure may be shortened to 12 or 16 hours. At the end of exposure, all doors and windows should be opened to provide as much ventilation as possible. Appropriate tests for lingering fumigant should be made with detector tubes or other suitable equipment to ensure that gas concentrations are below the threshold limit value before the building is reoccupied.

Automatic Injection

This type of application is confined to treatments of milling machinery. The fumigant is discharged in equal, predetermined dosages from special equipment operated by compressed air, which are supplied by the fumigant manufacturers or blenders (Figure 35). The liquid is injected through small holes specially bored at selected points in the milling machinery. Because this is essentially a machinery fumigation, the building may be fully ventilated during treatment.

Automatic injection in mills is a specialized treatment and details of dosage, location of injection points and other technical considerations are determined after an inspection of the premises has been made by representatives of the companies supplying the fumigants and the applicators.

A similar type of treatment has been used For the control of insects in the wooden linings of railway box cars (Dawson, 1962; Schesser, 1967).

FUMIGATION OF BAGGED GOODS IN SHIPS AND BARGES

Plant products in bags may readily be fumigated with methyl bromide while they are still loaded in ships and barges. If proper provision is made for the even distribution of the fumigant throughout the load any full cargo space may be fumigated. An important consideration is that in large spaces it may take some time to complete thorough aeration after treatment (Monro, 1947b; Markin, 1963). Treatment of bulk grain in cargo ships is discussed in Chapter 10.

Phosphine may also be used For treatments in barges if the longer exposure periods recommended For the use of this Fumigant are practicable. As stated in Chapter 6, due consideration must be paid to the presence of copper containing equipment in the structure. A procedure for the use of phosphine in combination with methyl bromide for the fumigation of bulk loaded expeller in barges and coasting vessels has been developed by Wohlgemuth et al (1976).

FUMIGATION PROCEDURE

Methyl bromide

The methyl bromide cylinders are placed on the open deck and Connected to copper or olyethylene tubing leading into the holds and ending in one or more T-shaped nozzles. At least one 25- or 30-cm (10- or 12-in) circulating fan should be placed as near as possible to the bottom of each hold and, when the gas is released, the fans should be operated for 30 minutes in order to prevent stratification and to aid distribution of the yes. Fans are also useful in hastening aeration after fumigation.

The penetration of methyl bromide is outstanding and the gas will escape unless adequate precautions are taken for sealing. A single ordinary canvas tarpaulin is not

sufficient to contain the gas during the fumigation period. However, three canvas tarpaulins in good condition are able to prevent leakage, especially if they are dampened. Suitable sizes of special tarpaulins with a plastic coating impervious to methyl bromide may be obtained to cover the hatches. If suitable or sufficient tarpaulins are not available, strips of tar paper joined together by various widths of brown paper glued with flour paste should be laid down above the hatches, with ordinary canvas tarpaulins then placed on top. Canvas tarpaulins usually provide sufficient cover for the ventilators.

Many modern ships have steel rolling hatch covers, called "McGregor type", which require no extra sealing for methyl bromide fumigation. These covers are lowered into place off their dollies onto a rubber gasket and the full weight is sufficient for a good seal. If the dollies are warped after rough use the side bolts may be used to pull them down into place.

When methyl bromide is used, the ships' officers, with their knowledge of the construction of the vessel, may be of great assistance to ensure that adequate sealing is obtained. They can point out possible sources of leakage, help check the ventilation system and openings between bulkhead on older ships and also see that hatch covers are secured properly (Monro, 1969).

<u>Phosphine</u>

Phosphine may be applied in barges loaded with bagged goods according to the procedures described below in this chapter for wheeled carriers.

PRECAUTIONS

If the cargo space of a vessel is fumigated while the ship is in port, it is recommended that the entire crew be evacuated while the fumigation is in progress. Warning notices should be prominently displayed at gangways and entrances to accommodations and a guard should be stationed at each gangway to prevent unauthorized persons from going aboard. No one should be allowed to return to quarters until the ship has been certified "gas free" by the fumigator in charge. Further information on the safety procedures recommended for fumigation of ships in port can be obtained from the Inter-governmental Marine Consultative Organization, MSC Circular 298, 23 January 1981 (IMCO, 1981) or to subsequent documents as they are updated.

SMALL-SCALE TREATMENTS

On board ship there may be rooms usable as fumigation chambers. Ammunition and other storage lockers are usually gas-tight and of sufficient size for treating small amounts of infested goods. Fumigation is conducted in the same way as in a regular chamber. Extra care must be taken during aeration because, in the absence of a proper exhaust vent, the gas will diffuse out through doors and portholes.

FUMIGATION OF EMPTY CARGO SPACES

Empty holds in cargo ships or on some passenger vessels often have residual populations of stored-product insects. If the infestation is localized, it can be controlled by spraying with a suitable insecticide. This method, however, cannot be relied upon for complete eradication. Usually, a complete fumigation is required (Monro, 1969).

Aerosols, which are fogs, mists or insecticidal smokes produced by various devices, have already been mentioned in the Introduction. They can be used to treat populations of stored-product insects in empty holds, and are satisfactory for killing the insects exposed in the open. Some information on the use of dichlorvos for control of insects in empty cargo ships is given by Bond et al (1972). However, all of these materials, including dichlorvos, have poor powers of penetration and are not as efficient as fumigants for obtaining complete control throughout the structure.

When a fumigant is used, one or two boards covering the bilges in each side of the ship should be removed. Piles of dunnage, if present, should be broken up to allow penetration of the gas from every side.

METHYL BROMIDE

Methyl bromide penetrates well into cracks, crevices and spaces under boards. In such places there are accumulations of grain and other foods in which the insect populations are able to multiply and from which they spread to the cargoes and other parts of the ship.

The fumigation of empty holds with methyl bromide follows the same basic procedure already described for loaded cargo spaces. Fans placed at the bottom of the holds are again absolutely necessary to give proper gas distribution. Recommended treatments are given in Schedule Q. It will be noted that dosages are lower and exposure periods shorter than those for loaded spaces.

To eradicate Irogoderma beetle infestations, more particularly Irogoderma qranarium Everts, increased dosages of methyl bromide are needed (Slabodnik, 1962; see Schedule Q).

HYDROGEN CYANIDE

HCN may also be used in empty holds although it does not diffuse very well through residual debris from plant products to reach deep-seated infestations. The most convenient method to apply HCN in ships is by means of the impregnated discs. These are often kept on hand for medical quarantine fumigation against rats.

With HCN, the general preparations and precautions are the same as for methyl bromide, with the following points of difference.

1. The ordinary canvas hatch tarpaulins, if in good condition, are satisfactory for HCN fumigation; it is advisable to use two to each hatch.

2. If fans are used for distribution of HCN within the hold, they must be explosion proof.

3. The discs are distributed as widely as possible in the hold by lifting the tarpaulins on each corner of the hatch in turn; this work is facilitated by removing the four corner hatch boards before the fumigation.

4. The tarpaulins are then battened down securely.

AERATION

Procedure and precautions for the ventilation of empty cargo ships are the same as already described for loaded ships. The gases diffuse more quickly from the empty holds and, under conditions favourable for aeration, the holds may be entered two or three hours after the hatches are opened.

RAILWAY CARS AND OTHER WHEELED CARRIERS

Some wheeled carriers may be used for fumigation. Treatment in such vehicles is often convenient and may show considerable economy in time and labour. By making a treatment of infested goods in a carrier, at least four manipulations, involving loading and unloading the vehicle and the fumigation chamber, are avoided. Furthermore, the fumigation kills the insects in the free space of the carrier and live pests do not remain behind to infest or invade the next load. In this way a great deal of possible cross-infestation may be avoided.

RAILWAY CARS

Railway companies are usually willing to permit fumigations in their equipment. It is, of course, essential to solicit their cooperation before treatments are planned.

In some countries, the standard railway cars (wagons) are well built and constitute in themselves excellent fumigation chambers; steel cars are especially suitable. Refrigerator-type cars, by the very nature of their construction, are usually gas tight if all openings are carefully sealed. (It is important to remember that in the cars using ice, drainage pipes from the ice bunkers should be plugged during the fumigation). In all railway cars, the wooden floor is likely to be the principal site of leakage. Some cars that are not sufficiently gas tight may be readily sealed by some of the methods already described. Also, 8 leaky car could be covered with a gas-proof sheet and fumigated, if a satisfactory seal can be made at ground level and around the rails. When railway cars are to be fumigated, they are usually isolated on separate sidings and kept there while under gas. This arrangement is, of course, essential if the cars are covered with sheets. In some countries, under certain circumstances, railway cars may

be allowed to travel while still under gas. Appropriate warning signs are placed on the main doors or hatches, with instructions for the adequate airing of the car before it is entered for inspection or unloading.

In France and in the United States, there are special fumigation chambers with railway tracks running into them so that the cars may be fumigated singly or in groups. Some of the chambers are designed for fumigation at atmospheric and others at reduced pressures. This arrangement has the advantage of allowing treatment of both the inside and outside of the vehicles, a consideration which may be important from the quarantine point of view, especially at border points.

The fumigation of railway cars under gas-proof sheets, as described above, may seem to eliminate the need of constructing permanent chambers. In plant quarantine practice, however, the choice of method against the threat of introduced pests should be made on the grounds of efficacy rather than of convenience or economy.

TRUCKS AND CARGO TRAILERS

Highway vehicles that can be rendered gas tight are suitable for the fumigating of goods loaded into them. In general, the same considerations apply as for railway cars.

For certain operations, the use of gas-proof sheets, particularly of the light-weight polyethylene type, is a convenient and effective improvisation. In this work, the trucks or trailers may be driven onto a gas proof groundsheet and then covered with another sheet, which is sealed to the lower one with snakes in the usual manner, thus providing a gas proof structure around the vehicle.

FREIGHT CONTAINERS

Fumigation of many commodities is carried out in freight containers and other transport units that are designed for carriage on vehicles. The procedures for treatment of these containers are much the same as for railway cars and cargo trailers. They may be fumigated while stationary or the treatment may be continued "in transit". Procedures for fumigation of tobacco with phosphine in freight containers, along with efficacy of the treatment, have been outlined by Childs et al (1971).

If the freight containers undergoing fumigation are to be loaded on ships, the guidelines given by the Inter-governmental Maritime Consultative Organization (IMCO, 1981, or subsequent recommendations) should be followed.

FUMIGANTS FUR CARRIER TREATMENTS

In practice, methyl bromide and phosphine are the materials most commonly used for wheeled carriers containing plant products, because these two yeses penetrate effectively into many commodities. Ethylene dibromide was used successfully in the United States for truck fumigation in the campaign against the Mediterranean fruit fly

in Florida. Truckloads of oranges were run into atmospheric chambers equipped with ducts specially designed for circulating the fumigant/air mixture through the load (Grierson and Hayward, 1959).

APPLICATION OF FUMIGANTS

In general, the techniques of sealing sod fumigant application are the same as those already described for the atmospheric chamber or gas-proof sheet fumigations.

Methyl bromide

Fumigation of bagged grains, meals and other plant products in carriers, such as railway cars, is easily done with methyl bromide in cans (0.45 or 0.68 kg) or in steel cylinders. This fumigant should always be applied from outside a railway car using 6 mm (0.25 in) polyethylene or copper tubing attached to the cylinder or to the special opener/applicator designed for cans. The tubing is inserted through a crack between the door and door frame, through a roof vent or possibly through a hole drilled in the floor. The discharge end of the tube is plugged sod a hole drilled through both walls 3-4 cm below the tip, then the end of the tube is attached close to the ceiling at the centre of the car, so that the methyl bromide mist can be directed over the commodity and toward both ends of the car.

The dosage to be applied is determined according to the size of boxcar as well as the temperatures of the atmosphere and the commodity. Temperatures above 10°C with exposure periods of 12 to 18 hours are recommended for this treatment. After applying the proper dosage the tubing is withdrawn and the opening sealed. At the end of the fumigation period all doors and vents are opened to allow as much circulation as possible. At least 30 to 60 minutes are required to aerate the free space of the car, but appropriate detecting equipment should be used to make sure that no methyl bromide is present when personnel enter to unload the car. Respiratory protective equipment should be worn when checking for fumigant in the car.

Phosphine

Various formulations for generating phosphine are used in fumigating railway cars and other carriers. Tablets or pellets of aluminium phosphide may be used by placing them in moisture-permeable envelopes and attaching these at intervals to the wall of the carrier or placing them in shallow cardboard boxes on top of the load (Schoenherr et al, 1966; Schesser, 1967). To avoid the possibility of combustion, only two tablets or ten pellets should be inserted in each envelope. Prepacks, with pellets appropriately separated from one another in a specially prepared plastic strip and covered with permeable paper, are supplied by some manufacturers for convenient application of the fumigant. They ore sometimes attached to the inner side of the door just prior to closing and sealing. If sachets are used they may be strung by a thin rope above the load. Lochner (1964b) gave a full description of the use of aluminium phosphide tablets for the fumigation of maize in bags or in bulk while in transit in railway cars.

Magnesium phosphide in tablets, pellets or embedded in moisture-permeable plastic plates is also available for use in a similar way.

PRECAUTIONS

The general precautions for railway cars and freight containers are similar to those already recommended for buildings and ships.

If a line of cars is being treated, it is advisable to put the usual gas warning sign on a special stand, which is staked in a conspicuous spot beside or between the railway tracks at each end of the line. Railway sidings chosen for holding cars during fumigation should be at least 100 m from any dwelling or building regularly occupied.

Where in-transit treatments are carried out, warning signs should be placed in conspicuous locations near each door of the carrier. They should be firmly fixed so that they are not easily lost or removed before the car or container is opened for aeration. For such in-transit treatments the warning signs should indicate the date of fumigation as well as the type of fumigant. Prior to unloading of fumigated vehicles, appropriate tests should be made to ascertain safety of the cargo area.

The success of in-transit fumigations is particularly dependent on good construction of the railway car or freight container and effective sealing methods.

FAN CIRCULATION

Fan circulation is essential in carrier treatments for fresh fruit, vegetables, plants and nursery stock when using a fumigant such as methyl bromide. This is to ensure proper evaporation and distribution of the fumigant in treatments of short duration (2 to 4 hours).

In fumigation of bagged grain and plant products, the exposure periods are at least 12 hours. If the fumigant is evenly distributed above the load at the time of application, subsequent fan circulation is unnecessary.

BULK GRAIN TREATMENTS

Fumigations of bulk grain may be carried out in railway cars and in well built trucks. The principles and techniques are essentially the same as for bulk grains in flat storages (as described in Chapter 10). Alumirlium phosphide tablets applied by probes or sachets inserted in the bulk may be used. Liquid type fumigants have also been used in open-top transit trucks with the grain being covered with a gas-proof sheet after application. A canvas tarpaulin can be used as an additional cover (Gray et al, 1964).

Gaseous-type fumigants such as methyl bromide, may also be used if provision is made for adequate recirculation with special equipment (see Phillips and Latta, 1953; USDA, 1963).

INDIVIDUAL PACKAGE FUMIGATION

Techniques for applying small doses of a fumigant to individual bays, packages or other containers show considerable promise for use either in emergencies or where conventional fumigation equipment is not available. There are at present two factors which may assist the development of such methods for practical use. First, some modern packaging materials are sufficiently gas tight to retain the vapours for the length of time required for successful treatment. Second, there are fumigants which can be applied conveniently to containers and which also have physical properties, such as slow evaporation or diffusion, that are suitable for this purpose.

In India, ethylene dibromide was injected into grain, stored in jute bags, at the rate of 10 ml per bag. This either killed the insects present or drove them out (Pingale and Swaminathan, 1954). Experiments with injection of four other fumigants into insecticide-impregnated jute bags containing grain confirmed the greater efficacy of EDB for this purpose. Control was not complete in non-impregnated bags (Muthu and Pingale, 1955).

The use of small cardboard discs held in aluminium foil, as described in Chapter 6, has been found useful for bag treatments (Muthu, 1964). These discs are illustrated in Figure 36. In Ghana, EDB was successfully used on individual jute bags with polyethylene liners as described in Chapter 6 (Hall, 1˚63).

It should be noted that EDB is now considered to be hazardous to human health and, therefore, care should be taken to ensure that no one is exposed to its vapours and treater) grain should be thoroughly aired so that residue is reduced below the FAD guideline levels (FAD/WHO, 1980).

In the United Kingdom, two tablets of aluminium phosphide were inserted individually into bags of wheat and rye resting on gas-proof sheets. One tablet was placed near the middle anti one near the mouth of the hag. Tablets were deposited either by hand or with a special probe dispenser. The gas proof sheets were then wrapped over small groups of bays and well overlapped. After five days of exposure, the sheets were removed. This treatment gave good control of a representative collection of species of stored-product insects and mites, although some adults of the granary weevil, Sitophilus qranarius, survived in cold wheat used in one test. It appears that this method holds promise for treatments of sacked grain in farm storages or other places where little special skill is required. for the control of certain insect species, such as the granary weevil, the dosage per bag should be increased to three tablets (Heseltine and Thompson, 1957).

Using polyethylene-lined sacks, Proctor and Ashman (1972) achieved good control of insects in bags of groundnuts being transported from Zambia to the U.K.. When a 0.6 9 aluminium phosphide pellet was applied in jute or woven polypropylene sacks of 32-82 kg capacity and lined with polyethylene 63.5127.5 µm thick, the c x t product for phosphine exceeded 50 mg h/l, and 10C percent mortality of all stages of the test insects, including Sitophilus zeamais Mots. was recorded. Although many liners in sacks split during transportation, this did not affect the efficiency of the phosphine fumigation or permit reinfestation.

PACKAGING LINE TREATMENTS

Treatments on the packaging line are of concern at present in the food processing industries, and the subject falls more in the realm of industrial rather than agricultural practice. Some discussion of the techniques is given here, not only because they are interesting examples of how fumigants may be used, but also because similar methods might be applied to solve more strictly agricultural problems.

Packaging line treatments have helped to keep certain food products, such as dried fruit and vegetables, free from infestation as they leave the processing plant (Simmons and Fisher, 1946). The technique is applicable when the packages are made of materials, such as cellophane and fibreboard, through which fumigants do not diffuse very quickly. The fumigants are dispensed into the individual packages from automatic machines, which can be calibrated to give an accurate dose. Application may be made before or after the contents are placed in the package. The best stage is just before the package enters the unit which seals the wrapping. The wrappings generally used are sufficiently gas tight to maintain an insecticidal concentration of the fumigant long enough to kill any insect stages present in the package.

To protect plant workers, exhaust hoods, approved by health authorities, should be installed to draw fumes away from the working area (Mayer and Nelson, 1955). Also, appropriate analytical tests should be made to ensure that threshold limit values for the fumigants are not exceeded. Experience has shown that fumigants diffuse away from the packages fairly rapidly after application, sometimes within 48 hours. Thus, it is considered that these treatments do not create any hazard to consumers.

Fumigants used for this type of application include methyl bromide, ethyl acetate, ethyl formate and propylene oxide. In the past, methyl bromide has been mixed with high proportions of carbon tetrachloride for package treatments.

Propylene oxide and ethylene oxide are also applied to certain packaged foods, especially dried fruit, to prevent microbial spoilage and to control insects.

Dosages for packaging line treatments vary greatly according to the product, material used for packing, method of packing and fumigant used.

9. VACUUM FUMIGATION

In vacuum fumigation, most of the air in the chamber is removed before the fumigant is introduced. It is, therefore, necessary to have a specially constructed chamber, usually made of steel, that is capable of withstanding external pressure up to one atmosphere. The installation also includes a pump able to evacuate the chamber in not more than 10 to 15 minutes, and valves and pipes for introduction and exhaustion of the fumigant. A vacuum fumigation installation is illustrated in Figure 37.

The primary object of vacuum fumigation is to hasten and improve the penetration of the fumigant into the material undergoing treatment. It was originally developed for this purpose when hydrogen cyanide (HCN) was the principal fumigant used. The advent of methyl bromide and phosphine, with their greater powers of penetration into many materials, made vacuum fumigation less important for the treatment of certain commodities.

Today, the technique is used chiefly in plant quarantine work (Richardson and Balock, 1959) and for fumigating tobacco (Tenhet, 1957) and other materials, such as compressed bales of jute bags (Monro and King, 1954) and pressed dates (Brown and Heuser, 1953a), which are difficult to penetrate at atmospheric pressure. It is also used in some food manufacturing industries for the fumigation of packaged cereals and prepared foods.

The fact that a vacuum treatment may be completed in 1.5 to 4 hours, as opposed to 12 to 24 hours for atmospheric fumigation, may commend it for use when a quick turnover of goods is necessary, as, for instance, at a busy seaport.

Vacuum fumigation cannot be used with certain tender plants, fruits and vegetables which are unable to withstand reduced pressure.

A vacuum fumigation installation is considerably more expensive than an atmospheric chamber of the same capacity. The decision as to whether the vacuum technique should be adopted should be made by weighing the possible advantages against the greater cost of installation.

FUMIGANTS

The number of fumigants which may be safely and conveniently used in vacuum fumigation is strictly limited on account of various technical considerations. The materials principally employer) at present, in approximate order of importance, are:

1. <u>Ethylene oxide/carbon dioxide mixture</u>, which has a wide use in the food industry for treating processed and unprocessed foods. With considerably increased dosages it is also used for sterilizing food. It can also be used for sterilizing other materials, but this is outside the scope of the present manual; for general reviews of gaseous sterilization see Rauscher et al (1957); Bruch (1961).

2. Methyl bromide, as a general purpose fumigant in this field.

3. Hydrogen cyanide, formerly widely used but replaced largely by ethylene oxide and methyl bromide.

IMPORTANT. **Under no conditions should phosphine, generated or dispensed in any manner, be used in vacuum fumigation. This compound is unstable at reduced pressures.**

METHODS

In recent years, considerable research has been undertaken on the methods of conducting vacuum fumigation for obtaining the best results with certain fumigants used on certain materials.

Basically, there are two main methods: sustained-vacuum fumigation and nearly complete restoration of the pressure, either simultaneously with the introduction of the fumigant or some time later (Page et al, 1953). The choice of one of these methods depends to some extent on the material being treated. Thus, fruit, vegetables and growing plants are usually completely ruined if they remain exposed for more than a few minutes to a pressure below 250 mm (10 in) of mercury. Seeds, grains, cereals and dry plant products are generally able to withstand these low pressures without ill effects.

SUSTAINED VACUUM FUMIGATION

The pressure in the loaded chamber is reduced to between 25 to 150 mm (1 to din) of mercury. The fumigant is then introduced, causing usually only a small rise in pressure. No further alteration is made to the pressure in the system until the end of the treatment which may last for 1.5 to 4 hours, at which time atmospheric pressure is restored by allowing air to enter. The fumigant/air mixture is then pumped out. The cycle of air introduction and evacuation may be repeated several times, A process referred to as "air washing", until it is considered safe to open the door for unloading (Page et al, 1953). This method is used widely all over the world for treating tobacco, grains, flour and meals. Even in this type of vacuum treatment, gas distribution may not be entirely uniform; some chambers are equipped with recirculating systems and others with fans. Some living plants are able to tolerate sustained vacuum treatments at pressures in the region of 380 mm (15 in) of mercury. Such treatments may be useful in the control of borers or other insects inside stems or other plant tissue.

A substantial number of dormant, non-foliated plants, roots and bulbs can be fumigated safely under a sustained vacuum of 100mm (4in) at an exposure period of 2 to 3.5 hours, as shown in Schedule F. In some cases, a higher vacuum can be used without injury.

ATMOSPHERIC PRESSURE RESTORED

Following the creation of the initial low pressure, atmospheric pressure may be restored in the chamber in several different ways, which may be summarized as follows:

1. Gradual restoration of atmospheric pressure. The required dosage of fumigant is discharged and air is then slowly introduced until a pressure just below atmospheric is reached after 2 hours in a 3-hour exposure period (Monro, 1958b).

2. Delayed restoration of atmospheric pressure. Following discharge of the fumigant, the vacuum is sustained for about 45 minutes and the air is introduced rapidly into the chamber (Brown and Heuser, 1953a, b, 1956; Monro and King, 1954).

3. Immediate restoration of atmospheric pressure. After the fumigant is discharged, atmospheric pressure is rapidly restored in the system by opening one or more valves leading into the chamber. This method, rather unscientifically described as the released vacuum or dissipated vacuum method, has been used extensively in North America for the fumigation of baled cotton (USDA, 1915).

4. Simultaneous introduction of air and fumigant. In this technique, special metering equipment is provided whereby the fumigant is introduced simultaneously with air so that 8 constant proportion of fumigant to air is maintained until the entire dosage has been introduced (Lepigre, 1949).

At the end of the treatment by any of these procedures, sir washing is carried out as described above for the sustained vacuum technique.

In a series of experiments using compressed bales of jute containing larvae of the cadelle, Tenebroides mauritanicus, it was found that the relative efficacy of these four methods, from the viewpoint of insect mortality, was in the same order as listed. In effectiveness, the sustained vacuum technique occupied an intermediate position, immediately below method 2. The results of these experiments are summarized diagrammatically in Figure 38 (Monro, 1958c).

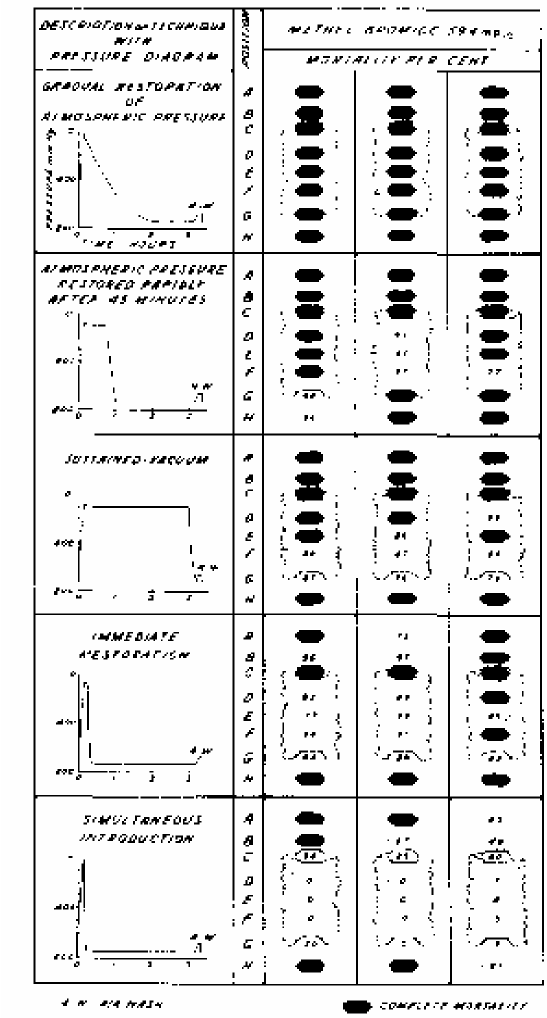
It must be emphasized that, while the information given here may be useful as a guide for the investigation of vacuum fumigation techniques, each problem will have to be solved separately, due consideration being given to the commodity involved, the species of insects and their stages and the climatic factors in the country where the work is being done.

EQUIPMENT

A detailed discussion of the structure and operation of available mechanical devices for vacuum fumigation is not given in this manual. Each manufacturer supplies the information pertaining to his product. Some information on the construction and

performance standards of vacuum fumigation chambers has also been given in Sec. IV – Part 1 of Plant Protection and Quarantine Manual (USDA, 1976). In Countries where the method is used, the responsible scientific authorities would work out treatments they consider best for dealing with their own particular problems.

FIGURE 38 – Diagrammatic comparison of mortalities of larvae of Tenebroides mauritanicus (L.) in five methods of vacuum fumigation of compressed bales of jute bags at 25°C. facie bale contained 300 bags and measured 50 x 50 x 60 cm.



(Monro, 1958c)
Locations are:
A. Upper free space
B. On top of bale
C. Inside top bag
D. 12 cm from top surface
E. Centre of bale
F. 12 cm from lower surface
G. Underneath bale
H. Lower free space

Some suggested vacuum fumigation treatments are given in Schedule P. They are to serve mainly as a guide in the operation of small chambers of less than 25 m^3 (1 000 ft^3) capacity for plant quarantine purposes.

10. FUMIGATION OF GRAIN IN BULK

The fumigation of sacked grain was discussed together with that of stored products in Chapter 8, because the techniques for the treatment of all sacked materials are basically the same. On the other hand, the fumigation of grain stored in bulk presents special problems of gas distribution, and it is necessary to deal with this subject separately.*

Fumigants are used for disinfesting grain in most countries of the world. The chemicals used and the methods of application vary greatly. Differences in technique may be influenced by the nature of the crops and by the wide range of climatic conditions encountered. The effect of type and condition of grain on the efficacy of fumigation has been described by Harein (1959). One of the most important variables lies in the diversity of structures used for storage. The shape, size and type of construction of each particular structure create special problems in achieving and maintaining the concentrations required for the control of the insects and mites present in the grain.

The more important grain-infesting insects are cosmopolitan; they have been transported through international commerce to many parts of the world. A treatment effective in one country may therefore be successfully adapted in another if due allowance is made for the variables mentioned in the preceding paragraph. The relative amount of destruction caused by certain species varies somewhat from continent to continent or from country to country. Therefore, the most serious pests of grain may differ in their order of importance from one area of the world to another.

The dosages of the various fumigants as given in Schedules A and B are recommended as guides. Experience gained in a given country, or under specialized conditions, may indicate the need for modifications.

It was stressed in Chapter 2 that there are great variations in the susceptibility of insects to different fumigants, not only among species, but also between stages within a given species. Treatments given in this chapter should be adequate to deal with all insect species and their stages which feed and develop inside or outside the grain. Additional dosages may be needed for special conditions. All stages of the Khapra beetle, Troqoderma qranarium, other beetles of the genus Trogoderma, and the cadelle, Tenebroides mauritanicus, show exceptional resistance to ethylene oxide and to halogenated hydrocarbon fumigants, such as methyl bromide, ethylene dibromide and ethylene dichloride. When these insects are present in the grain, it is advisable to double the dosages given in Schedules A and B of fumigants containing these ingredients. On the other hand, these insects are quite susceptible to hydrogen cyanide and additional treatment is not needed with this fumigant.

* Contact insecticides are often applied to grain as it is run into storage. The use of these is often subject to rigid governmental regulations on account of the poisonous residue problem. There are wide variations in practice or in regulations in different countries. Formulations containing pyrethrins, malathion or other insecticides are permitted by some governments. A detailed discussion of these insecticides is outside the scope of this manual.

A number of different techniques are described here, some of which are peculiar to certain countries or districts. From this selection, suitable applications may be adapted or devised to solve local problems.

It should be pointed out that in some countries there are strict government regulations concerning the choice of materials that may be applied to grain for disinfestation purposes. The treatments discussed in this chapter have been practiced in some countries, but not necessarily in all. Before grain fumigation is undertaken, therefore, it is necessary to make sure that the use of the chosen material is not against the regulations of the country where the treatment is to be carried out or of any country to which the grain may be exported.

When a storage place is partly full, insects may be present not only in the bulk of the grain but also on the walls. If control is to be effected solely by fumigation, the dosage should be the same as for a full storage. As an alternative measure, contact insecticides may be applied to the walls either as a spray or as a smoke if appropriate means are used for preventing the contamination of the grain. If only the grain needs to be fumigated, the method of surface application described below may be used. If the moisture content of the grain is not high, the surface of the mass may be covered with a gas-proof sheet to prevent the vapours from diffusing upward into the empty space.

As already stated, the shape and size of a given storage unit are important considerations. Grain storage units are usually broadly classified for fumigation purposes as follows:

1. Upright (vertical) storage. In this type, the height is greater than the length or width. It is mainly found in the form of silo bins in storage units with elevators. In cross-section the bins may be almost any shape but are usually circular or rectangular.

2. Flat (horizontal) storage. One dimension, either length or width, is greater than the height. This type includes a wide variety of structures, including many temporary (sometimes called "distress") storage units. Railway freight cars (wagons) or motor vans (trucks or lorries) may be included under this heading.

3. Farm-type bins and storage units. These are usually small and often loosely constructed and their treatment requires special consideration.

In the following description of methods of grain fumigation, mention will be made of special applications suited to these three types of storage.

METHODS OF GRAIN FUMIGATION

The differences between methods of grain fumigation are related primarily to the type of fumigant initially applied to the grain mass. Gas-tight structures that will retain a sufficient concentration of fumigant for the required period of time are essential for effective treatments. For the fumigant phosphine, gas tightness is particularly important because this gas can penetrate to escape much more easily and rapidly than other fumigants. The standard of gas tightness recommended by the Australian Committee on Agriculture (Winks et al, 1980) for fumigation with phosphine requires structures to be sealed so they can maintain an excess internal pressure from 500 Pa (2 in water gauge) to 250 Pa (l in water gauge) for not less than 5 minutes in filled structures of 300 to 10 000 tonnes capacity. The roofs of structures sealed to this standard must be painted white to reduce thermal expansion of the atmosphere within the headspace.

In the case of phosphine it is essential to maintain uniform concentrations for sufficient periods of time to kill all insects present; high dosage rates do not compensate for inadequate standards of gas tightness with this fumigant. The objective of the fumigation must be complete control of all stages of all species of pest so that resistance to the fumigant does not develop.

DIRECT MIXING (VERTICAL STORAGE)

By this method, the fumigant is applied to the grain so that it is distributed as evenly as possible from the beginning of the treatment. Direct mixing is often employed when infestation is general throughout the mass and when there is access to the grain stream during filling or transfer from one bin to another. Only solid or liquid-type fumigants are used in this way. Fairly even distribution of the gas with good control of the insects can usually be obtained.

The solid-type fumigants used for this treatment are aluminium phosphide tablets or pellets evolving phosphine and granular calcium cyanide evolving hydrogen cyanide. Aluminium phosphide tablets or pellets can be inserted in the grain stream by hand or with an automatic dispenser calibrated to deliver a dosage appropriate to the rate of loading in the bin (Figure 39). Calcium cyanide is usually discharged from an automatic applicator. Also, aluminium phosphide powder formulation in paper bags may be added to grain as bins or silos are filled. In this case, it is necessary to provide for removal of the bags after fumigation is complete.

A convenient method for applying bags of aluminium phosphide to grain in vertical storages involves a permanently installed system of pipe-, fixed vertically to the walls of the bins or silos (Anon, 1980). With this system the fumigant is applied in long narrow bags 22 x 6 cm, by hooking the bags to a chain at prescribed intervals and

suspending them in the pipe. There are caps at both ends of the pilling system; the top cap is equipped with a coupling to retain the chain holding the fumigant bags and the bottom cap is threaded for easy cleaning of the pipe. Small portals in the piping permit the fumigant to diffuse out arid penetrate into the grain mass. This system eliminates the need for turning the grain to disperse the fumigant and allows easy removal of the bags of expended dust residue after the treatment. It should be noted that this system is not designed for tablets or pellets of aluminium phosphide and could be hazardous if high concentrations of the gas evolve in a confined space.

Liquids may conveniently be applied to the grain by means of ordinary watering cans with the sprinklers left on or by means of ordinary piping or tubing of not more than 1 cm (0.375 in) internal diameter. The required dosage for each lot of 1 000 bushels (36 m) of grain may be applied from one sprinkler can to each lot as it passes on the heft. If necessary, by prearrangement with the weigher, there can be a one- or two minute break between 1 000 bushel drafts. This arrangement also enables the fumigator to keep a check on even application of the fumigant. In upright storages of grain, in order to ensure adequate distribution at the top and bottom of the mass, an extra dosage at the rate required for 1 000 bushels may be placed at the beginning of the run for the first 1 000 bushels and the same amount sprayed or sprinkled on the surface of the grain mass to control surface infestation.

Storage bins of the vertical type usually have manhole covers in the ceiling and these are usually closed immediately to prevent loss of fumigant. If there is no roof to the storage unit, the grain should be covered with a gas proof sheet of the type already described in Chapter 8.

For this work there are also available automatic applicators which apply the liquid continuously or intermittently. It should be pointed out that devices merely emptying drums with a preset discharge valve are inaccurate, because the pressure of the liquid above the valve varies from the time the container is full until it is almost empty, and a higher proportion of the dosages is therefore discharged into the grain at the beginning of the run. The only reliable automatic device is one employing a gear pump equipped with a bypass so that there is a constant pressure of the fumigant on the discharge orifice, the excess fumigant being returned to the drum. In this way, the fumigant is applied to the grain stream at a constant rate of discharge according to the dosage required.

Precaution. In the application of fumigants to grain streams, care should be taken that fumes are not inhaled. Liquid-type fumigants are especially hazardous because vapours may be given off before the grain enters the storage.

Warning. When grain fumigants are atomized or sprayed into closely confined spaces, or into a shallow space above the grain surface, the concentration of fumigant may exceed 2 percent by volume in air. Canister-type respirators will afford no protection under these conditions. It is better for the fumigator to remain outside and to apply the fumigant through an opening (see Chapter 3 Figure 8). If it is absolutely necessary

for operators to enter such a space during fumigations, air-line or self-contained respirators should be worn.

As the grain enters vertical storage units, currents of air containing fumigant vapours may be forced up into the working space. Operators may therefore be exposed to fumes even when working outside the structure being treated. Under these circumstances, it may be necessary to wear respirators fitted with the proper canisters.

Many modern silos have windows running along either side of the head house, and these should be kept open whenever possible so that a good cross-draught of fresh air is produced. Under such conditions of good ventilation, respirators need not necessarily be worn; however, gas detection equipment can be used to ensure that harmful levels of fumigant are not present.

Dosage and Exposure

Dosages of fumigants recommended for the mixing-in-grain technique are included in Schedules A and B. Dosage in fumigation of grain by direct mixing is modified by the kind of grain treated and the gas tightness of the structure. Wind forces, thermal expansion of the internal gas and changes in atmospheric pressure can also influence gas loss from storage structures (Mulhearn et al, 1976).

The dosages in the schedule shown for upright storage units apply to steel or adequately gas tight concrete bins. The rates should be doubled for wooden bins. Unless specifically mentioned in the text or schedules there is no definite exposure period in this type of fumigation. However, the grain should be left undisturbed for at least 72 hours. The usual practice is to leave the grain for a much longer period so that the fumigant vapours are gradually dissipated by leakage from the structure. Fumigants applied and left in this way should not contain ethylene oxide.

The importance of proper aeration of fumigated grain used for seed especially under tropical conditions, is demonstrated by the work of Caswell and Clifford (1958) in Nigeria. An ethylene dichloride and carbon tetrachloride mixture (3:1) was applied to maize in jars, which were immediately sealed with air-tight lids, according to the local custom. Although the actual germination of the seeds was not significantly affected, root and shoot development of young plants was seriously impaired when the maize was kept sealed under fumigation for more than one month.

SURFACE APPLICATION (FLAT STORAGE)

The surface application method has so far been used mainly with liquid type fumigants. The liquids are sprayed evenly over the top surface of the grain and the vapours slowly evolve and diffuse downward through the bulk. This method is usually employed only when the grain cannot conveniently be turned or as an emergency measure.

Diffusion may be slow and distribution with some fumigants is often not uniform. Carbon tetrachloride has given good distribution in grain in deep bins in the U.K. following a single surface application, and there are a number of standard fumigant mixtures which have been used for this purpose. Less hazardous substitutes for carbon tetrachloride, such as methyl chloroform, may be used for this type of treatment in the future. Unmixed carbon disulphide has been used in many countries, although its tendency to burn or explode is well known. Propylene oxide has been used in France and Algeria. In this type of treatment, the grain is usually not aerated and the vapours remain in the grain until dissipated by leakage.

The fumigants usually recommended for this type of work and suggested rates of application are summarized in Schedules A and B.

The selection of methods of application of fumigants to the surface of stored grain is influenced by the size and type of storage. Methods are therefore discussed under two main headings: large hulk fumigations and small or farm type storage fumigations. In all storage units with all techniques, the fumigants diffuse more evenly through the moss when the surface of the grain is level. Therefore, if at all possible, every reasonable effort should be made to level the grain surface before the fumigant is applied.

<u>Large Bulk Fumigation</u>

The liquid-type fumigants are usually applied to the surface of bulk grain by means of sprayers. If the surface area is large, power sprayers may be used. If possible, application should be made from outside the bin or storage through a manhole, roof hatch, window or door. However, in large Flat storage units it may be necessary for the operator to walk across the surface of the grain as shown in Chapter 3, Figure 9.

In treating large bulks of grain by surface application, extraordinary precautions, over and above those already mentioned, should be taken to protect the operators The men applying the fumigant should wear airline or self-contained oxygen or compressed air respirators.

With all types of sprayer the nozzles are removed to facilitate the rapid application of the liquid to the surface of the grain. for bulks up to 30 000 bushels, a sprayer which delivers the liquid at the rate of 35 to 55 1 (8 to 12 gall) per minute is suitable. This may be effected by using a bronze gear pump operating at about 90 revolutions per minute in conjunction with a 3.5 hp gasoline engine or the power take-off from a tractor. For larger bulks, adequate hose and a pump capable of throwing a stream about 25 m (75 ft) at the rate of 450 1 (100 gall) per minute should be used.

Hazards to personnel applying liquid fumigants in large flat storages may be greatly reduced if the grain is sufficiently level to permit sleds to be drawn across the surface from one end to the other. The spray nozzles may be placed on a spray boom mounted on the sled and adjusted to distribute the required dosage in an even spray on both

sides as the sled is pulled across the storage by means of a rope or chain. If the storage space is wide, two or more sleds should be pulled simultaneously across the surface so that the operators can leave the building immediately after the fumigant has been applied.

Methyl bromide

Although methyl bromide is sometimes considered impractical for surface application, when deep penetration of a grain mess is involved, it has been successfully used for such purposes. Ooffe and Nolte (1957) fumigated a large bulk of maize 5 m deep in a flat storage unit measuring 70 x 60 m using gas proof plastic sheets. The fumigant was applied at the rate of 48 9 per m for an exposure of 24 hours in a grain mass where the temperature varied from 11 to 22°C. It was discharged under the gas-proof sheets over the surface of the grain from 64 evenly spaced outlets in polyethylene tubing connected to two 70 kg cylinders of fumigant.

A method for treatment of high vertical bins of grain by applying methyl bromide with carbon dioxide has been developed by Calderon and Carmi (1973) . The carbon dioxide acts as a carrier and will take the methyl bromide down through the grain mass to the bottom of the bin. Carbon dioxide from blocks of dry ice or from pressurized cylinders is applier) at the surface of the grain with the methyl prornide. When the dry ice is used, blocks 1 - 2 kg in size are spread over the surface of the grain and the methyl bromide is released through a garden sprinkler or, preferably, through a spray nozzle that is positioned centrally on the surface of the grain. When carbon dioxide in pressurized cylinders is used it is released simultaneously with the methyl bromide. Special cylinders have been developed to allow sufficiently rapid release of carbon dioxide (2 .6 kg/min) and it is vaporized by passing through a hot water vaporizer. Dosages of 50 g/m^3 methyl bromide and 200 - 250 g/m^3 carbon dioxide at 20°C and above are used.

It has been found that the downward movement of the carbon dioxide-methyl bromide mixture into the grain may be so rapid in some treatments that the concentration in the upper layers is reduced to give a low c x t product; in such cases the dosage of carbon dioxide should be reduced by 10 - 20 percent. If the bins are properly sealed, the internal pressure may rise 10 15 cm on a water gauge due to expansion of the gases.

This method has been used successfully for ten years as a routine treatment of grain in vertical silos in Israel (Navarro, 1981).

Phosphine

In flat storage units, in which the depth of the grain does not exceed 10 m (about 30 ft), tablets, pellets or sachets containing aluminium phosphide may be used. To simplify application, it is advisable to level the surface of the grain as much as possible before the work is begun.

The fumigant is usually applied by probing into the grain (Figure 40). Probes specially designed for the purpose are used to insert the fumigant into the grain, bet under farm conditions ordinary 2 .5 cm (l in) diameter iron pipe may be used (Watters, 1967). The number of tablets or pellets used per probe is determined by dividing the total amount of fumigant to be used by the number of probing to be made. For large areas of grain surface, a convenient method for measuring the distances for application is with a rope or stout cord, marked at appropriate intervals, stretched from opposite walls. In most storage units where there is considerable air space above the grain bulk, or when it is considered that significant loss of fumigant may occur above the load, it is advisable to c over the entire mass with gas-proof sheets.

Large masses of grain may also be treated by distributing the fumigant over the surface and covering with gas-proof sheets to allow the gas to diffuse into the grain. McGregor and White (1969) have successfully fumigated stacks of bulk cottonseed 32 m long, 20 m wide and 10 m deer' in this way. Analysis of gas concentrations showed that the phosphine diffused throughout the mass of cottonseed and an appreciable concentration was still present 120 hours after the fumigant was applied. Wainman et al (1974) described the successful fumigation, using pliosphine, of 750 tonnes of wheat in inflatable butyl rubber silos.

Large quantities of grain can also be treated in the holds of cargo ships in an "in-transit" shipboard fumigation procedure. Redlinger et al, (1979) found that good dispersal of the gas and control of insects was obtained when aluminium phosphide tablets were spread on the grain at intervals during the loading operation (i.e. when the hold was 33, 67 and 95 percent full). In these treatments the fumigant is allowed to remain in the grain during the voyage of the ship and until the cargo is removed.

Note. When fumigants are used for treatments on ships the guidelines given by IMCO (1981, or subsequent recommendations) to provide for safety of the ship's crew end longshoremen should be strictly adhered to.

FARM STORAGE FUMIGATION

The gas tightness of the structure is particularly important in small storages, because the mass of grain is not large enough in itself to retain vapours once leakage begins at any point. Steel, concrete or tight wooden structures are usually satisfactory without alterations. For small cracks or openings a caulking gun may be used to apply compounds that will give a semipermanent gas-tight seal. Most wooden storages are leaky and it may be necessary to line the floor and walls on the inside with stout roofing paper or plastic sheeting and to nail boards over any visible openings in the walls. If it is inconvenient to move grain, the paper or plastic sheeting may be applied to the outside of the bin or building, but this is not as effective as an inside lining. If possible, do not fumigate during windy weather because strong air currents hasten leakage.

Experience has shown that results are not usually as good in small bulks of grain as in large bulks. One reason is that there is often a poor kill on the top surface. Also, in small bulks good control is more difficult through the mass in grain that is "tough" or has excessive dockage.

The use of aluminium phosphide tablets has proved effective for the treatment of small storages. See discussion above for details of this method. If aluminium phosphide is used, it is recommended that a tarpaulin or polyethylene sheet be placed carefully over the surface of the grain after the tablets are applied.

The best way to apply a liquid fumigant to small storages is by spraying the surface from the outside of the building with the aid of a stirrup pump. Some liquid fumigants, such as chloropicrin, are supplied in l lb (0.45 kg) cans or bottles. In some applications, it is convenient and satisfactory to puncture the cans or open the bottles, invert them and thrust the opening about 15 cm (6 in) below the surface of the grain. It is recommended that the openings be stuffed with wads of cotton or cellucotton to prevent too rapid loss of the liquid, but loosely enough to produce a wick effect that will allow the liquid to flow gradually into the grain. This method permits accurate and economical distribution of the dosage since the required number of containers may be spaced evenly on top of the grain.

Piles of grain, large or small, may be treated by surface application in any of the ways described above. However, only partial kills may be expected if the grain is not covered with 8 gas-proof sheet either before or immediately offer application of the fumigant. This method should be attempted only in calm weather.

At best, fumigation of piles outdoors is a temporary expedient. If at all possible the grain should be moved into a storage or carrier and treated in a more effective way.

SURFACE INFESTATION

With certain species of insects, such as the Indian meal moth, Plodia interpunctella (Hbn.), infestation may be confined to the top of the grain. This problem cannot be solved by the usual method of surface application of fumigants because the vapours diffuse down through the grain, and it would thus be necessary to treat the whole mass at great expense in order to deal with grain near the surface. Also, turning the grain only spreads the infestation throughout the entire bulk of grain. In silo bins or other storage units, which can be made air tight above the grain surface by closing manholes and other openings, surface infestations can be treated with materials such as dichlorvos to obtain control, particularly infestations of some of the moths, Slow release resin strips that will give off 20 mg dichlorvos per m per week have been found to give satisfactory control of moths in granaries (Schmidt and Wohigemuth, 1979). Surface sprays of dichlorvos may also be used; in this type of application appropriate precautions regarding exposure of personnel should be taken.

For storages with ventilators, where dichlorvos vapour may be lost, an aerosol emission system has been found superior to the slow release strips (Bengston, 1976). Using a dosage of 1 g dichlorvos per 100 m , released at daily intervals, satisfactory control has been obtained in commercial storages in Australia. The safety and reliability of the system were found to be satisfactory.

It should also be pointed out that incipient surface infestations of insects may be arrested by using pyrethrum, malathion or other approved materials applied as a fine mist in the space over grain. Ultra low volume sprayers that produce very fine particles of spray give good results.

"HOT SPOT" FUMIGATION

Treatment of localized areas in a grain mass is often a useful technique for dealing with incipient infestations. These "spots" are usually recognized and defined by a local rise in temperature. Liquid-type fumigants applied through tubes or aluminium phosphide tablets are the best materials to use. In this type of work the tendency is to underdose. Enough fumigant should be applied to maintain the required lethal concentration, not only in the region of infestation, hut also in the margins surrounding it for I or 2 m (3 to 6 ft) in every direction (Note: Results are improved if the marginal applications are made first in a ring surrounding the "hot spots", followed by those applier) to the spot itself. The vapours from the marginal treatments tend to slow down diffusion of the fumigant from the infested spot.) For liquids applied in a flat or farm-type storage, 8 good rule is to use enough to treat the known area and also the grain from the surface to the floor.

Methods of application and dosages are the same as for surface applications.

RECIRCULATION

For the treatment of bulk grain, recirculation of the fumigant by means of permanent or temporary installations provides an effective and economical means of insect control. This method was first investigated in Europe in connexion with the development of fixed installations for drying grain in silo bins. Subsequently, it has been widely adopted for use in grain silos and with fixed or temporary drying equipment. One of the more important advantages of the method is that lengthy exposure periods are unnecessary. In addition, distribution of fumigant throughout the grain mass may be improved.

Recirculation is only practicable when the walls of the storage units are sufficiently gas tight to prevent the fumigant/air mixture from being forced out while under positive pressure from the blowers. Many concrete silos may be used without further alteration, but with some it has been found necessary to apply sealers to the inside walls. For this purpose, the best materials are an internal bituminous coating covered by two layers of rubber-based paint.

In addition to its use in permanent installations, recirculation has been successfully improvised as an emergency technique, especially for dealing with problems associated with the long-term storage of crops. Many diverse structures used for grain storage have been fumigated, including oil storage tanks, cargo ships, Quonset huts, cottonseed storage tanks, conventional silo bins and ordinary steel railway cars.

The recirculation method is usually advocated for methyl bromide, hydrogen cyanide or liquid type fumigants but it has not been recommended for phosphine. Because mixtures of phosphine and oxygen may produce explosions at reduced pressures, considerable care has been taken in the past to avoid procedures that might bring about such effects. However, test treatments with phosphine in large grain storages have shown that this fumigant can be dispersed more rapidly and uniformly by a recirculation procedure to give more effective and economic treatment than other methods (Cook, 1980).

The procedures used for recirculation of phosphine are in the developing stages and may be subject to variation and refinement in the future. Possible hazards that may arise in employing this technique are not fully known and require further investigation. As both these procedures and the precautions needed for recirculation of phosphine are somewhat different to those developed for other fumigants, they are outlined separately after discussion of the older established methods.

Fixed Installations

Permanent recirculation systems designed for fumigants other than phosphine and of the type illustrated diagrammatically in Figure 41 are most useful in grain silos at ports or other transfer points where grain is not stored for lengthy periods. The structure and operation of such equipment will not be discussed in detail; this information is furnished by the engineering companies which design the equipment according to the needs of each particular establishment.

Temporary Adaptations

Recirculation methods have been devised for utilizing existing aerating systems in storage units. This is effected simply by providing some means of returning the air which has passed through the grain back into a blower so that continuous circulation is achieved. A similar system for fumigation only may be installed in a storage not already equipped for aeration.

Although the air flow rates in a given aeration system are considerably reduced by the addition of a return duct, the blowers used are adequate to provide the required flow of fumigant/air mixture.

In existing aeration systems, recirculation may be effected in the following ways:

1. By provision of portable flexible tubing which may be connected at the bottom to the aeration duct in the hopper and at the top by means of a specially constructed duct leading through the manhole or other opening into the top of the storage; the portable tubing and upper duct can be moved to any storage bins requiring treatment (Figure 42).

2. Where several adjoining bins are used, a single metal duct can serve as the return and be joined through the top and bottom manifolds to any bin as required.

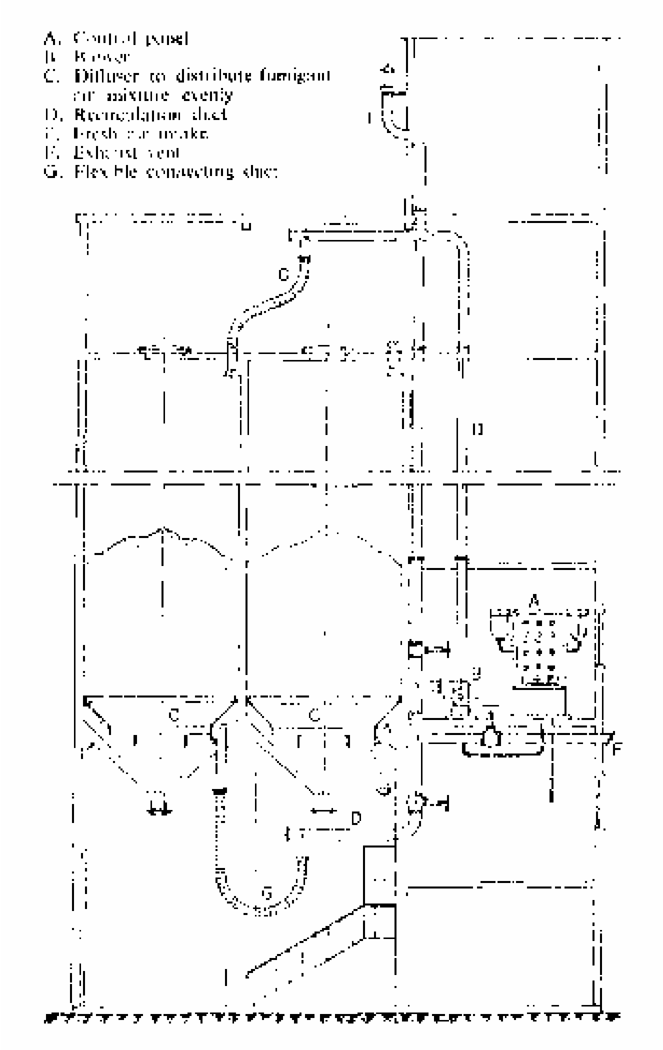
3. An empty bin can serve as the return duct if suitably connected to an adjoining infested bin; however, use of this may necessitate extra fumigant to maintain full concentration throughout the system.

4. Two filled and infested bins can be connected and treated at the same time, the fumigant being drawn down through one and up through the other.

Where there is no existing aeration system, a perforated plate can replace the gate in the unloading spout, a duct run from this plate to the blower and a duct or flexible tube run to the top of the bin, thus completing the circuit. In that arrangement, the static pressure is likely to be high, but a portable blower of sufficient power can be provided.

The gaseous-type fumigants may be recirculated upward or downward through the grain according to convenience or an existing direction of flow. In practice they are usually released into the system near the blowers.

FIGURE 41. - Permanent installation for fumigation of grain in silos by recirculation.(Societe anonyme Mallet)



<u>Air Flow Requirements</u>

In the design and installation of fumigant recirculating systems, advantage may be taken of knowledge already obtained in the study of the aeration of stored grains. There are four basic factors influencing the design of such systems.

1. A rate of air flow through the grain adequate both for circulation of the fumigant and cooling of the grain is 1 litre of air per minute for each 50 1 of grain (0.025 ft per minute for 1 bushel).

2. The air flow through grains varies according to the species and condition of the grain. Shedd (1953) has published a chart from which the pressure drop per foot depth of various grains may be read in terms of inches of water. These values may be used to calculate the total resistance to air flow of a given depth of grain in storage. When the grain has been stored for some time, it will pack and a "pack factor" is applied to the calculation to allow for this.

3. The ducts offer resistance to air flow. Charts are available in standard heating, ventilating and air-conditioning guides or manuals for calculating the friction loss in ducts for different air flows. Factors are given for calculating additional resistance at elbows in the ducts.

4. It is necessary that particular attention be paid to the provision of a well-designed air distribution system at the bin bottom; otherwise there may be an excessive loss of pressure at this point. Even with satisfactory systems using large distribution cones, antigrading devices or perforated grills, the loss of pressure at the point of entry of the air into the bin bottom may be larger than the fall in the rest of the column of grain. This is due to the high air velocity at this point compared with that higher up in the bin where the flow is more evenly distributed over the cross-section.

With calculations based on these four factors, it is possible to determine the capacity of a blower capable of bringing about the required air flow in a system consisting of a given storage and the ducts attached to it.

The gaseous-type fumigants are best suited for the recirculation technique and are usually discharged into the system just behind the blower. Liquid type fumigants are not usually recommended in this type of application, except in case of emergency. Liquid types (if used) may be sprayed over the grain surface before the recirculation starts.

Dosages

The rates of application for the fumigants recommended for use with recirculation are given in Schedule A.

Exposure

In the average silo bin, 15 to 20 minutes are required to replace the original air by the fumigant/air mixture. Unless the system leaks, it is advisable to recirculate the gas/air mixture at least two, and preferably four or five times. This will ensure the thorough mixing of air and fumigant in all parts of the grain mass.

At the end of 24 hours (the usual maximum exposure period for this type of treatment), the duct is disconnected from the top of the storage and the blower is operated for at least three hours while the fumigant vapours are driven into the open air above the structure.

Detailed Calculations

Fumigant manufacturers supply booklets and brochures containing detailed information on how to carry out the necessary calculations outlined above, together with recommendations for the types of blowers and other equipment needed.

FORCED DISTRIBUTION

Application of methyl bromide and some of the liquid-type fumigants has been made in storages without modifying existing aeration systems. By operating the blowers, fumigant applied at the top of a storage may be drawn down to the bottom or when introduced at the bottom, may be forced up to the surface. It is necessary to have the means to determine when the gas/air mixture has reached the bottom or top of the mass. This may be done for methyl bromide and liquid-type fumigants containing organic halides with the aid of a thermal conductivity gas analyses, or even with an ordinary halide leak detector. When liquid-type fumigants are used, it has been the practice, especially if a thermal conductivity analyser is available for checking, to force the vapours back to the surface every 24 hours.

With this technique, at the end of the required exposure the residual vapours are partially exhausted into the open air by means of the blowers. However, by the process of desorption, the fumigant concentration may build up in the intergranular air spaces, and exhaustion by blowers may have to be repeated a number of times at intervals of several hours.

Because this method is simple and does not require the extra ducts needed for the recirculation, it appears, superficially, to offer an inexpensive and convenient method of grain fumigation, especially as no modification of existing aeration systems is required. However, it has been found that the method, referred to as "forced distribution", has several disadvantages both in theory and in practice. These are concerned principally with difficulties in obtaining even distribution of the fumigant as compared with the ordinary recirculation technique described above.

When this method is used, dosages are based on those recommended for recirculation in Schedule A, but it is probable that these would have to be increased by at least 50 percent.

RECIRCULATION PROCEDURES FOR PHOSPHINE

Two procedures have been tested for the recirculation of phosphine in grain storages. The first, which has been successfully used in a number of trials, employs extremely low air flows to give a complete air change within the grain mass in 8 to 12 hours (e.g. approximately two air changes within the 18to 20-hour period required to release phosphine from the tablets). For example, a large tight steel or concrete storage bin would have a small return pipe (ca 150 mm diameter) connected from the top of the bin to the inlet of a 2 hp blower and then to the aeration system at the bottom of the bin for circulation of the fumigant. Aluminium phosphide tablets or pellets at the recommended rate are broadcast over the surface of the grain before the bin is sealed. When the concentration of phosphine in the headspace has reached 300 - 600 ppm, the blower is activated to circulate the gas through the grain mass. Concentrations of 320 - 340 ppm have been found dispersed throughout the entire grain mass within 12 hours of the first day of treatment with this technique. The blower should be run for

24 to 30 hours, with the fumigation continuing for at least three days and preferably for five days. Using this method, it is claimed that the dosage of fumigant can be reduced and the exposure time shortened substantially (Cook, 1980).

The second method, which has been developed only recently, uses a probe inserted in the grain to carry the fumigant down and through the grain mass. A small aluminium probe, perforated with 3 mm holes in the lower 4.5 m, is pneumatically drilled into the grain and a small high speed blower fixed at the top to carry the fumigant-air mixture down through the probe. The fumigant-air mixture brought in from the headspace over the grain is introduced on the suction side of the blower and is blown down the probe to disperse laterally and displace the intergranular air in the grain. With this method the fumigant was found to radiate out from the probe at a relatively uniform concentration in a 3 350 tonne bin of grain in 24 hours of blower time (Cook, 1980).

GENERAL SAFETY PRECAUTIONS

The application of fumigants to large masses of grain in various types of structures and storage units involves the dispensing of considerable amounts of fumigant. Under these conditions, safety measures are of prime importance, not only to protect the operators, but also those working in the vicinity. It is also necessary to ensure that all fumigated grain is thoroughly aerated before it is released to customers or consumers. It is therefore considered advisable to recapitulate the precautions required.

Operators. Only fully trained and qualified operators should be entrusted with the fumigation of grain in commercial storage units and installations. Most countries have national or local regulations covering the licensing of operators. Some manufacturers require that persons using their products receive the required training and they provide facilities for this. Such stipulations often do not apply to the use of fumigants at farm level. These are usually small-scale treatments and are often carried out by the farmers themselves; however, adequate instructions on both methods of application and precaution should be given.

Application. The operators must be fully protected at the time of application. This is especially important in connexion with liquid-type fumigants. Proper ventilation of the working space where the materials are being applied is most necessary.

Other persons working in the vicinity must be warned that a fumigation is in progress. Appropriate warning signs should be posted wherever necessary.

Recirculation and forced distribution. While circulation and distribution of the fumigant are being undertaken, persons working in the building or in adjoining ones must know that these operations are in progress and take the necessary precautions to protect themselves.

Careful checks should be made of all recirculation equipment, fixed or temporary, to ensure that there is no significant leakage of the fumigant from any part.

SAFETY PRECAUTIONS FOR PHOSPHINE

In addition to the general precautions necessary for all fumigants, special care should be exercised with phosphine to avoid subjecting it to any condition that might produce fire or explosion. It must be stressed that this fumigant can be employed safely under normal conditions of fumigating without undue hazards; fire or explosions are not likely to be produced in conditions normally recommended in fumigation procedures. However, phosphine will react with oxygen to produce Flame or explosion at high concentrations and also over a range of low pressures.

The spontaneous flammability of phosphine is well known. Commercial formulations are designed to release the gas slowly so that the concentration remains well below the flammability level. However, manufacturers advocate caution against any practice that will cause rapid release or allow high concentrations of phosphine to build up.

1. Formulations should never be allowed to come in direct contact with any liquid, particularly water, as this may cause rapid release of the gas.

2. No formulation should be used under any condition which will allow the gas concentration to reach the lower level of flammability (1.79 percent by volume). It should never be confined in small gas-proof enclosures, such as plastic bags, nor should it be packed in envelopes or dumped in piles where excessive levels of the gas could build up.

In addition to flammability at 1.79 percent, phosphine can react with oxygen to produce an explosion at lower concentrations if it is subjected to reduced pressures. In carefully controlled experiments with pure materials and very low pressures, phosphine has been found to combine with oxygen in an explosive chain reaction (Dalton and Hinshelwood, 1929). This reaction is promoted by other gases, including nitrogen and carbon dioxide, but it seems to be reduced by moisture.

The possible significance of this reaction to the use of phosphine in recirculation systems is not known at this time. Experimental evidence suggests that the reaction occurs at pressures well below those expected in commercial recirculation systems. however, until all of the conditions that will promote the reaction are known, great care should be taken in any treatment where phosphine might be exposed to pressure changes. Further research and development on all aspects of the procedures, including investigations on the conditions produced in recirculation systems (e.g. pressure changes, the presence of dust and other gases, etc.) are needed before it can be generally recommended.

AERATION

Aeration procedures vary according to the fumigants used and the type of installation. Methyl bromide, chloropicrin and hydrogen cyanide should not be kept in the grain beyond the prescribed exposure periods. It is also not usually recommended that

aluminium phosphide be left on the grain beyond normally recommended exposure times. Exposure periods for all grain fumigations are given in Schedules A and B.

Liquid-type fumigants containing ethylene dibromide, ethylene dichloride and carbon disulphide in admixture with carbon tetrachloride or chloroform are often left on the grain until the normal turning procedure is undertaken. The vapours tend to dissipate gradually during this process.

After completion of the required exposure period in ordinary-type silos and elevator bins, the grain is turned onto the belts and elevators and transferred to a new bin. In recirculation and forced distribution systems, fixed or temporary valves are opened or ducts disconnected, at the top of the silo bins and the blowers are operated for 3 to 4 hours to blow fresh air into the grain and thus ventilate the fumigant from the mass. In all these aeration procedures precautions must be taken to protect people in the vicinity so that they are not exposed to the fumes as they are being exhausted.

On the completion of treatment of smaller amounts of grain, such as in farm storage units or under sheets, no elaborate procedures are required. It is usually only necessary to allow fresh air to gain access through all available openings and to allow this aeration to continue until the residual vapours have completely dissipated. Residues of aluminium phosphide will sooner or later be removed from the grain by turning.

Special care should be taken to ensure that adults, children and animals are not exposed in any way during this time.

When any of the above aeration procedures are satisfactorily completed, at least 24 hours should elapse before the grain is released to consumers or processors. At temperatures below 15°C, longer waiting periods should be enforced to ensure that the final small amounts of residual vapours have been dissipated.

SELECTED LITERATURE

Grain fumigation is a broad subject. What may be considered basic information and principles have been presented in this chapter. There is a steady flow of publications on this subject in national and international journals and in the official government publications of many countries. Valuable and specific information is sometimes only available in instruction booklets and brochures put out by fumigant manufacturers. The following literature references should be consulted as a guide to sources of more detailed information, on recirculation and forced distribution:

Berck (1975); Brook and Redlinger (1954); Brown and Heseltine (1949); Cotton and Walkden (1951); Holman (1960b); Howe and Klepser (1958); Lindgren and Vincent (1960); Monro (1956); Philips (1952, 1955, 1956, 1957b); Phillips et al (1953); Phillips and Latta (1949, 1953); Redlinger (1957b); Sergeev et al (1965); Storey (1967, 1971a, 1971b); Whitney and Kenage (1960).

11. FUMIGATION AND CONTROLLED ATMOSPHERE STORAGE

In addition to the poisonous gases that are used for pest control, the normal gases of the atmosphere can be altered to achieve control. The use and manipulation of natural components of the atmosphere, e.g. oxygen, nitrogen and carbon dioxide, to preserve food is referred to as "controlled" or "modified" atmosphere storage. Controlled atmosphere techniques are widely used in the storage of perishable commodities such as fruit, vegetables, cut flowers, etc. to retard ripening and reduce spoilage from micro-organisms. Also, they will control some insects in these products (Morgan and Gaunce, 1975; Aharoni et al, 1981). The most extensive use of controlled atmospheres for insect control is on grain and similar commodities. Here the atmospheres are modified by removing the life-supporting oxygen or by adding high levels of carbon dioxide.

Although the principle of modified atmosphere storage has been used since antiquity, e.g. in hermetic storages, a number of procedures have been developed in recent years to replace the normal atmosphere of a storage for the purpose of controlling pest organisms. In many respects the practice of using modified atmospheres for insect control is closely related to fumigation. Gas-tight enclosures are required, many of the procedures are closely related and the problems are often similar to those found in fumigation. When carbon dioxide is used, it is applied as a fumigant and it functions in a similar way.

Controlled atmosphere procedures are an appropriate substitute for the fumigation of some commodities because the gases involved do not leave harmful residues and often the atmospheres provide superior conditions to normal storage in air. In some cases the two procedures may be used in a complementary way to increase effectiveness of a treatment; carbon dioxide increases the toxicity of a number of fumigants to insects (Jones, 1938; Kashi and Bond, 1975).

Since sound pest management should, where possible, promote programmes that integrate appropriate control procedures and minimize the use of toxic chemicals and also since many of the requirements for fumigation are similar to those needed for controlled atmospheres, a brief account of controlled atmosphere procedures is given here.

BASIC REQUIREMENTS

Controlled atmosphere systems depend on either depletion of oxygen to asphyxiate organisms or the addition of carbon dioxide to act directly and kill them. In these treatments the new atmospheres are maintained for an adequate period to kill all stages of the organism, and they should have no adverse effect on the commodity. To achieve this the treatment requires:

- a storage structure capable of containing the gas;

- a source of suitable gas or a means of producing the required atmosphere;

- a method of maintaining the atmosphere for the required period of time;

- a method of aerating to remove the altered atmosphere after the treatment.

It should be noted that the controlled atmospheres, which are toxic to pest organisms, are also dangerous to humans and precautions are necessary to ensure that no one is exposed to them without special protection. Although nitrogen itself is non-toxic to humans, the absence of oxygen or the presence of high levels of carbon dioxide is lethal.

LOW OXYGEN ATMOSPHERES

Oxygen deficient atmospheres are produced by flushing a storage with nitrogen to displace the normal nitrogen-oxygen atmosphere. Liquid nitrogen from tanks may be used as a gas source (Banks and Annis, 1977). Exothermic inert atmosphere generators that consume the oxygen to leave principally nitrogen have been tested and show promise for insect control (Storey, 1973). These generators burn propane or other hydrocarbon fuel to give an atmosphere of less than 1 percent oxygen with about 10 percent carbon dioxide and 89 percent nitrogen. Oxygen can also be removed by the metabolic activity of micro-organisms and insects in hermetic storages, thus producing an atmosphere where insects cannot survive.

For complete insect control the level of oxygen must be maintained below 1.2 percent for one week, at temperatures above 35°C, or more than 24 weeks at 15°C (Table 15).

TABLE 15. SUGGESTED EXPOSURE TIMES FOR COMPLETE [)ISINFESTATION OF GRAIN AT LESS THAN 12 PERCENT MOISTURE CONTENT, WITH ATMOSPHERES OF 0 1.2 PERCENT OXYGEN IN NITROGEN.

GRAIN TEMP. (°C)	EXPOSURE TIME (WEEKS)
15	24
18	15
20	6
23	4
26	3
30	2
35	1

Source: Banks and Annis, 1977.

CARBON DIOXIDE ATMOSPHERES

Insects are generally killed more rapidly by carbon dioxide than they are by lack of oxygen. A concentration of 6n percent carbon dioxide will give over 95 percent control of most stored grain insects after a four day exposure at 27°C or higher (Jay, 1971); however, longer periods are needed for complete kill. Banks (1979) suggested that an initial level exceeding 70 percent carbon dioxide and maintained above 35 percent for ten days is appropriate for complete insect control at temperatures above 20°C.

The carbon dioxide gas is applied to storages from a vessel of liquid carbon dioxide with appropriate vaporizers and pressure regulators to control flow rate (Jay and Pearman, 1973). Carbon dioxide in the form of dry ice has also been used for the treatment of grain in freight containers (Banks and Sharp, 1979; Sharp and Banks, 1980) and in conjunction with fumigation of grain with methyl bromide (Calderon and Carmi, 1973).

GAS TIGHTNESS REQUIREMENTS

Structures used for controlled atmosphere treatments must have a high degree of gas tightness for the process to be effective and economical. They must be of sound construction and suitably modified so that gross gas loss through apertures, such as ventilators, open eaves and imperfections in the fabric, is prevented. Changes in temperature, atmospheric pressure and wind forces can have a pronounced effect on gas loss from the storage structure. For storages of 300 to 10 000 tonnes capacity a gas tightness that corresponds to a decay time of 5 minutes for an applied excess pressure drop of 2 500 to l 500, 1 500 to 750 or 500 to 250 Pa in a full storage has been found satisfactory (Banks et al, 1980). This specification corresponds to a whole area of no more than 1.0 cm^2(0.16 in.2) in a 2 000 tonne storage.

Gas is added to maintain concentrations at the required level in a storage over the entire exposure period. One of the main reasons that gas loss occurs is the diurnal temperature variation in the headspace of storage structures. This is less in concrete structures than in unprotected metal bins. Diurnal temperature fluctuations can be reduced by insulation, painting with a highly reflective white paint or by placing a false roof on the bin to leave a ventilated air space next to the permanent roof.

SEALING PROCEDURES

In structures other than welded steel, e.g. concrete, bolted or riveted metal, sealing of the entire fabric of the structure may be necessary. Bolted metal bins can be sealed by treatment of each lap joint and bolt location with silicon rubber sealant, thixotropic acrylics or by application of liquid envelope, "cocoon" type, polyvinyl chloride coatings. Concrete surfaces also may need to be coated with a good sealant that will prevent yes loss and protect the concrete from high levels of carbon dioxide. The permanent sealing of a 16 000 tonne capacity shed for fumigation or modified atmosphere storage of grain has been described by Banks et al (1979).

In bins that are very tightly sealed, some precautions are necessary to avoid unusual stresses on the structure caused by external or internal pressure changes. To prevent such changes in a bin that is sealed for a controlled atmosphere treatment, a pressure relief valve must be installed. If the bin will withstand the pressure, an operating level of + 1 000 Pa (4 in water gauge) appears to be suitable. Lower levels can be used but they should not be less than + 250 Pa. A simple U-tube valve of 8 cm (3 in) I.D. tubing with a liquid trap provides a convenient and fool-proof venting system (Banks and Annis, 1977).

TESTING FOR GAS TIGHTNESS

Structures can be tested for gas tightness using a pressure test system (static testing or pressure decay testing) or a procedure using carbon monoxide as a tracer gas. The pressure decay system is satisfactory for routine testing of bins and is given in some detail here. Further information on testing of storage structures for gas tightness may be found in the publications by Banks and Annis (1977) and Banks (1982).

To test a sealed structure by the pressure decay method, air is introduced by the gas introduction system from a blower capable of producing 6 m/min (212 ft^3/min) at 2 500 Pa (10 in water gauge). Pressure differentials can be measured conveniently on a portable water gauge similar to that shown in Figure 43. If a pressure of 2 500 Pa cannot be reached with such a blower, there may be too much restriction between the blower and the bin or the bin is less gas tight than required (e.g. 3.1 m/min at 2 500 Pa for a 2 000 tonne bin). Care should be taken to ensure that pressure within the bin does not exceed the engineering limitations of the bin or of the sealing that is used. When a pressure of 2 500 Pa or the design limit is achieved, air input is cut off in such a way that no air is lost back through the blower. Pressure decay on the water gauge is then related to the period of time involved.

PROCEDURES FOR ESTABLISHING CONTROLLED ATMOSPHERES

Controlled atmosphere storage can be viewed in two phases - the "purge phase" where the normal atmosphere is replaced with the prescribed atmosphere and the "maintenance phase" where the atmosphere is maintained for the desired period of time (Banks and Annis, 1977).

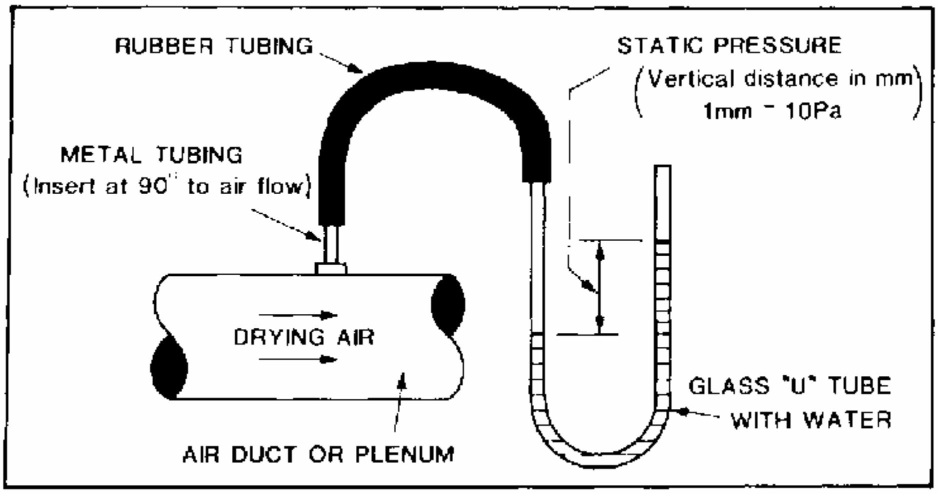
NITROGEN ATMOSPHERE

Purge Phase

Liquid nitrogen supplied directly from a road tanker is passed through a heat exchanging facility where it is vaporized and brought to ambient temperature. It is then passed through a flow meter (e.g. "Rotameter") into the gas introduction system of the bin. Five cm (2 in) I.D. PVC drainage piping can be conveniently used to carry the gas. A flow of 3 m/min (106 ft^3/min) has been found to be suitable for purging of bins from 300 to 7 000 tonne capacity, although this rate may be substantially increased

(e.g. to 8 m3/min) in bins fitted with aeration ducts modified to introduce gas. However, when gas in introduced directly into the bin at the walls, an increased input rate may be less efficient at lowering the oxygen tension. In cases where a low efficiency distribution system is used, pockets of air may remain which are not purged directly but in which the oxygen is removed through the slower diffusive and convective forces. In these instances a slower purge rate allows these processes to occur and is not wasteful of gas.

FIGURE 43. Water gauge for static testing or for pressure decay(Friesen, 1976) measurements.



A vent of at least 50 cm²(10 in) must be left open in the roof during the purge to prevent dangerous pressure build-up.

It is important that the heat exchanging facility is adequate to bring the gas close to ambient temperature (within 2°C). Cooling of the grain near the introduction point may result in moisture migrating to the cold area on long storage and is also detrimental to the insecticidal efficiency of the process. At 3 m /min (106 ft³/min) three Forced draught heat exchangers in parallel using 0.4 kW (0.5 h.p.) fans, with an atmospheric exchanger downstream in series, have been found to be just as effective. If icing occurs downstream of the exchangers, the input flow must be reduced.

Gas input must continue uninterrupted until the headspace has been reduced to about 1 percent O2. Purging in the grain mass occurs generally by the passage of a sharp front through the grain and direct displacement of the interstitial air. In the headspace where free gas mixing occurs, decay is exponential. When the headspace has reached 1 percent O2, the purge may be terminated, the top vent and introduction ports closed and the maintenance input of gas commenced.

The quantity of nitrogen required for the purge is strongly dependent on the ratio of the volume occupied by the bulk to the total storage volume (the filling ratio). Barley has a higher porosity and will require more nitrogen than wheat. In one trial with barley where the filling ratio was 0.80, a volume of 1.9 m^3 N2/tonne was consumed. At 3 m3/min the purging of a 2 000 tonne bin of wheat takes about 12 hours.

Maintenance Phase

After termination of purging, gas input at a lower rate is continued to maintain the atmosphere. The input rate required is determined by the bin capacity, its degree of gas tightness and the weather. At present it is best to adjust the maintenance rates by systematically reducing the flow of gas until the atmosphere is just maintained. At the correct rate, with grain temperatures exceeding ambient ones, the oxygen tension at the base of the bin will rise slightly during the day and fall to about 1 percent at night. The headspace tension should remain low. If the grain temperature is below ambient, or if the atmosphere contains more than 3 percent CO_2, effects will be seen in the headspace, not at the base.

The exposure periods recommended for different grain temperatures with 1 percent O2 in nitrogen have been given above in Table 15. These figures are tentative and subject to revision when further laboratory studies are completed. Sitophilus oryzae is one of the most tolerant grain pests in low oxygen atmospheres, and if there is any doubt about what species are present, the exposure for this pest should be used. In commodities where the pests are Tribolium spp. and Oryzaephilus spp. only, shorter exposure tames, half of those given, may he used. Currently available data for Rhyzopertha dominica are insufficient for an exact recommendation, but it is considerably more susceptible than Sitophilus oryzae and should thus be controlled by the exposures given. Exposure times should be based on the minimum temperature within the grain, not average temperatures. (For further details see Banks and Annis, 1977).

ATMOSPHERE FROM INERT ATMOSPHERE GENERATORS

A number of inert atmospher3e generators with capacities ranging from 1.4 m^3 (50 ft^3)/h to 2 800 m (100 000 ft^3)/h and capable of producing atmospheres with less than 1 percent oxygen are available on the market. Storey (1973) conducted tests in a 40 x 5.5 m (130 x 18 ft) silo containing 544 tonnes of wheat with two generators, each one capable of generating 420 m^3 per h of inert atmosphere (<0.1 percent 02' 8.5 – 11.5 percent CO2 plus N2). Using 3 cm (1.5 in) drain feeder pipes connected at the bottom of the bin, he was able to reduce the oxygen level throughout the bin to 1 percent or less in 48 hours. The oxygen deficient atmosphere moved upward through the grain mass with very little intermixing with the normal atmosphere at a rate about 2.4 m (8 ft)/h. In another bin that was purged with the inert atmosphere prior to filling with grain, the oxygen level throughout the bin, including the headspace, was reduced to less than 1 percent within 24 hours.

Similar tests were carried out by Navarro et al (1979) in welded steel bins containing about 1 200 tonnes of wheat with a generator producing exhaust gases at a rate of 144 m /h. When the generator was in a recirculation arrangement so that the gases were blown in through the roof of the silo and drawn back into the converter through a pipe at the base, the average oxygen concentration was reduced to 0.2 percent in 60.3 h (purge phase). During the maintenance phase, which lasted 21 days, the oxygen concentration was maintained below 2 percent by intermittent operation of the generator for a total of 19.5 h.

It should be pointed out that the moisture content of the wheat was affected by purging with this atmosphere, particularly in the upper layer at the region of introduction of the gases. A plastic sheet was placed below the point of gas entry to prevent moistening of the grain.

CARBON DIOXIDE

Grain Storages

Three procedures for establishing high concentrations of carbon dioxide in large silo-type bins have been tested by Jay (1980). These are based on introducing the gas at the top of a filled storage, at the bottom of the storage or with the grain stream during filling. A procedure for introducing the gas at the base of the storage with subsequent recirculation has been found to be effective in controlling a natural infestation of insects and is deemed to be commercially feasible (Wilson et al 1980).

For the latter treatment, liquid carbon dioxide supplied in cryogenic tankers is vaporized in a heat exchanger and the gas is diluted with air to give approximately 80 percent carbon dioxide and 20 percent air. The gas stream is maintained above 30°C with a superheater and introduced at the base of the bin through a 75 mm diameter iron pipe. When the carbon dioxide concentration at the top of the bin reaches a constant level, gas input is stopped and the atmosphere so established is recirculated through a 50 mm diameter plastic duct leading from the bin apex to the introduction port at the base. With the gas tightness standards specified above, this procedure will give a concentration of carbon dioxide >70 percent initially and this can be maintained at > 35 percent for ten days without requiring additional gas.

Freight Containers

Successful tests have also been carried out with carbon dioxide for disinfestation of freight containers loaded with wheat. In trials on gastight general purpose containers filled with commodity and dosed with 37 - 55 kg of crushed dry ice spread over the goods, plus 44 kg in blocks packed in insulated boxes, Banks and Annis (1980, 1981) found that the carbon dioxide level remained over 35 percent for a period of seven days or more and killed all of the test insects.

Tests have also been made for treatment of grain under gas-proof sheets with carbon dioxide (Banks and Annis, 1980).

TERMINATION OF TREATMENT

After a controlled atmosphere treatment is terminated, the modified atmosphere is gradually displaced by entry of air from outside. The rate at which this happens depends on a number of factors, such as gas tightness of the storage, contents of the storage and the weather, and it may be increased by making larger openings or by active ventilation with a blower. A 2 000 tonne bin with 5 cm (2 in) diameter openings at the top and base may reach acceptable oxygen levels of 16 percent from the established 1 percent in less than two weeks (Banks and Annis, 1977).

Care should be taken to avoid structural damage from the reduced pressures caused by rapid emptying of a tightly sealed storage. Steel bins have been severely damaged by rapid removal of grain without sufficient venting.

NOTE: Before emptying tightly sealed bins, open access doors or vents to allow adequate air to enter as grain is removed.

SAFETY PRECAUTIONS

Adequate precautions should be taken when working in areas close to controlled atmospheres or on entering storages that have been treated to avoid any harmful effects. Nitrogen atmospheres containing less than 14 percent oxygen or more than 5 percent carbon dioxide may be dangerous to human life. Personnel entering a nitrogen atmosphere containing less than 10 percent oxygen may collapse without warning and become unconscious. Carbon dioxide produces respiratory discomfort, light-headedness and nausea, and unconsciousness may occur in less than five minutes in 9 percent CO_2. In any case, where unconsciousness or respiratory distress occurs through exposure to a controlled atmosphere, the victim must be taken immediately to fresh air.

Portable oxygen monitors or carbon dioxide analysers should be available on the work site as well as air-line or self-contained breathing apparatus. Gas masks with canisters provide no protection against low oxygen or high carbon dioxide atmospheres. All enclosed working areas close to controlled atmospheres should be well ventilated and gas reservoirs should be kept outside if possible (Banks and Annis, 1977).

PROBLEMS ASSOCIATED WITH MODIFIED ATMOSPHERE STORAGE

In sealed systems, moisture may migrate and condense to produce problems, particularly in grain above 12 percent moisture content. High carbon dioxide or low oxygen atmospheres can inhibit mould and toxin formation and preserve germination under moist storage conditions. However, spoilage will occur once the modified

atmosphere is removed unless the grain is dried or processed within a short time (Banks, 1981).

Once the modified atmosphere is removed the commodity is open to infestation unless otherwise protected.

Grain kept under a modified atmosphere may develop taint; at higher moisture levels (> 16 percent) this taint may be difficult to remove (Banks, 1981; Shejbal, 1979).

High levels of carbon dioxide may cause structural problems in reinforced concrete storages by reducing alkalinity of the steel (Hamada, 1968). The significance of this reaction in grain storage is currently under investigation.

CHOICE OF TREATMENT

When a controlled atmosphere procedure is going to be used, the choice between using the nitrogen (oxygen deficiency) method or the carbon dioxide method may be determined by several factors. The amount of time available for the treatment, the suitability of the structure for holding the gas, the availability of the gases or equipment for producing them and the overall cost of the operation are all important. Carbon dioxide generally kills insects faster than nitrogen (oxygen deficiency) and requires a less stringent standard of gas tightness (Jay, 1980). The comparative cost of controlled atmosphere treatments will depend on the availability and cost of the gases, the amount required and transportation costs, as well as the costs of equipment and labour.

FUMIGATION, CONTROLLED ATMOSPHERES AND FORCED AERATION

The choice of treatment to be used for controlling insect infestations will vary with the type of problem and the relative merits of the treatment. Fumigants can usually be used effectively in storages prepared for controlled atmosphere treatments, as the standards of gas tightness that are required are generally more stringent for the controlled atmospheres. Also, the quantity of material required, the application costs and the exposure time are usually much less for fumigants than for controlled atmosphere treatments. On the other hand, controlled atmosphere procedures avoid the use of chemical pesticides, leave no harmful residues and can provide superior storage of grain. A combination of fumigation with controlled atmosphere procedures may have some potential, as the effectiveness of fumigants is enhanced by carbon dioxide.

In addition to controlled atmospheres, the forced aeration of grain is closely allied with insect control procedures and may be an integral part of a pest management programme. Calderon (1972) suggested that "a sensible use of ambient or chilled air for aeration of grain offers new possibilities in many parts of the world for preservation of grain without (or with very little) use of chemicals." The use of fumigants and controlled atmospheres together with forced drying procedures and aeration should be

considered as complementary conservation methods that form part of an overall pest management programme.

It must be pointed out that controlled atmosphere procedures are in early stages of development and progressive changes are likely to be made with further experience and research. A select bibliography on controlled atmosphere and aeration procedures up to 1981 is given below and may be referred to when extensive use of these procedures is planned.

SELECTED REFERENCES

CONTROLLED ATMOSPHERE TREATMENTS

Bailey (1955); Banks and Annis (1977, 1981); Banks et al (1979); Banks and Sharp (1979); Calderon and Carmi (1973); Hyde (1962, 1969); Jay (1980); Jay and Pearman (1973); Kruger (1960); Navarro et al (1979); Press and Harein (1966); Press et al (1967); Rannfelt (1980);'Sharp and Banks (1980); Shejbal (1980); Storey (1973); Vayssiere (1948).

AERATION AND FORCED DRYING

Armitage and Burrell (1978); Burges and Burrell (1964); Burrell (1967); Calderon (1972); Friesen (1976); Hearle and Hall (1963); Holman (1960a); Navarro (1976); Oxley and Wickenden (1963); Williams (1973).

12. GLASSHOUSE FUMIGATION

For many years, fumigants were used for the routine control of insect pests in glasshouses. Calcium cyanide dust, generating hydrogen cyanide (HCN) with the aid of the moisture of the air, and nicotine, volatilized as a gas by ignition or other means, were both commonly employed.

Recently, the aerosol method of dispersing insecticides and evaporation from steam pipes have found wide favour for glasshouse work, largely because considerable volumes of glasshouse space can be treated quickly and economically.

Although it was previously stated that the subject of aerosols lay outside the scope of this manual, it is impossible to discuss glasshouse treatments without taking into account the various ways in which the insecticides are dispersed. Therefore, a brief outline of the use of fogs, liquefied gas aerosols, smokes and actual fumigants will be presented with the intention only of indicating some of the general methods employed to control insects and related pests on plants in glasshouses.

CALCULATING SPACE VOLUME

In computing the dosage of insecticide to be applied, the cubic capacity of the glasshouse must be known. In calculating this, any space occupied by plants, benches, soil and other material should be ignored.

If the house consists of one span (lean-to-type), or is divided at the pitch of the roof into two even spans, the area of the cross-section may be calculated as the average height multiplied by the width. Thus, capacity of house = average height x width x length.

When the roof is of unequal span, it may be considered as consisting of two lean-to sections and the volume is calculated as the sum of these two sections.

PREPARATION FOR TREATMENT

When aerosols , fogs, smokes, steam pipe fumigants and gases are applied, it is necessary to close all vents. Temperatures should be maintained above 20°C but kept below 35°C. For this and other reasons, application is usually made in the evening. It is not practicable to carry out treatments when the wind velocity is above 16 kilometres (10 miles) per hour because when the wind outside is too strong, there is uneven distribution of the insecticide in the glasshouse, resulting in under dosing in some places and overdosing in others to the point of plant injury.

EXPOSURE TIME

The time of exposure for aerosols, fogs and smokes is usually two to three hours, after which all the vents are opened. By this time most of the material has dispersed or settled. However, when fumigation takes place with most of the available insecticides and acaricides (chemicals which kill mites), and with HCN generated from calcium cyanide, it is usual to leave the house under gas until early the following morning.

APPLICATION

Liquefied Gas Aerosols

In connexion with glasshouse work, the term "aerosol" is used to describe the form in which the insecticide is dispersed after it leaves a special cylinder (sometimes called bomb) in which it is dissolved in a volatile liquid held under pressure. On discharge into the open the liquid vaporizes and leaves the particles of insecticide suspended as a fine mist in the air. This form of application is distinguished from the generation of fogs and smokes.

A wide range of common insecticides and acaricides have been used for dispensing from small aerosol cylinders carried in the hand. These include such materials as lindane, malathion, dichlorvos (DDVP, Vapona) and DDT, used principally as insecticides.

Not all insecticides can be effectively dispensed from liquefied gases, because there are sometimes technical difficulties in finding suitable solvents and in producing formulations that do not cause clogging of the nozzles at the time of discharge. As a general rule, the toxicants with higher vapour pressures are more effective; this may be partly due to A fumigation effect (see Introduction). At present, too little is known about the mode of action of aerosols on insects and mites.

Before discharging the aerosol, many growers place the cylinder or bomb in warm water at, but not above, 38°C for half an hour or so. This increases the pressure in the container and thus gives better distribution when the aerosol is released.

Low cost. The aerosols are popular at present among growers because a glasshouse of 1 400 m (50 000 ft) volume may be treated in about three minutes at a very low cost.

Pests controlled. Aerosols are used to control many of the pests that attack glasshouse crops. However, aerosols cannot penetrate soil and they are not effective against slugs and snails. Scale insects are controlled to some extent but, for satisfactory results, treatments have to be repeated at regular intervals.

Precautions. Many of the materials used in aerosols are extremely toxic to human beings, including the carrier gases such as methyl chloride. It is necessary, therefore, that persons applying aerosols should wear a respirator and protective gloves and clothing. The respirator should be of the industrial type described in Chapter 3 and the canister recommended is for "organic vapours, acid gases, smoke and dust."

The protective clothing consists of a work suit completely covering the arms and body and long rubber gloves. After application is completed the protective clothing and gloves are removed and all skin areas exposed to the aerosol are thoroughly washed with soap and water. If operations are extensive, the working shoes should also be removed.

Warning. On no account should smoking be allowed in the vicinity while aerosols are being discharged or at any time during treatment until such time as the glasshouse has been fully aerated. Aerosols may be sources of fire or explosion; more particularly, methyl chloride is a highly flammable gas.

Smokes

Insecticidal and acaricidal smokes are particularly useful in smaller glasshouses. The toxicants are mixed with a combustible material in a special container, which allows ready ignition and discharge. These containers are usually tins or waxed containers and are popularly called "pressure fumigators" or "smokes". The range of materials available in this form is more restricted than in the aerosols. Azobenzene, nicotine, lindane, dichlorvos and others have been used.

Generally speaking, the smokes cause less plant injury than the aerosols and, therefore, the grower has to pay less attention to choice of material and to other technical considerations.

Warning. Smokes diffuse readily into offices and living quarters attached to glasshouses. **Care must be taken either to prevent diffusion or to evacuate such spaces while treatment is in progress.**

Fags

The production of "fogs" is, in effect, a modification of a spraying technique. By means of compressed air, spray concentrate solutions are forced through atomizers so that small droplets are formed. This method has been used for dispersing a number of insecticides and acaricides by means of portable fog-generating machines (Pritchard, 1949).

Gaseous Fumigation

True vapours or gases are still used in certain ways for glasshouse pest control.

Steam pipe fumigation. A method of some value is to paint a slurry of some toxicant on the steam pipes. The gas is usually volatilized during the night. The insecticide lindane has been used in this way and the vapours of naled (Dibrom) and dichlorvos have also been successfully used for the control of a large number of pests. In commercial application of both naled and dichlorvos, protective clothing and suitable respirators are required.

It is often necessary to repeat this type of treatment regularly once a week to obtain adequate control. (It should he mentioned that sulphur for the control of powdery mildew is often volatilized in this way or by using thermostatically controlled heating units.)

Calcium cyanide. HCN, generated from calcium cyanide, once very generally used, is still employed occasionally to solve certain problems or to serve as a variation of the aerosol technique. The form of calcium cyanide best suited for glasshouse work has the consistency of sea sand. Although moisture in the air is necessary for the generation of HCN from calcium cyanide, excessive moisture in the glasshouse cuts down the efficiency of the treatment by dissolving the gas; this may also lead to considerable plant injury. It is important that there should be no standing water on the walks where the dust is applied because a complex reaction takes place which reduces the amount of gaseous HCN given off. Therefore, it is the practice not to water the plants for several hours before fumigation.

Wearing a respirator with the special canister for HCN, the operator starts from the far end of the house and works toward the final exit door at the opposite end. He carefully pours a thin stream of cyanide from the tin container onto the concrete floor of the house taking care always to move away from the dust and never to cross back over a place already treated.

The dosage of calcium cyanide varies according to the pests to be controlled and the susceptibility of the varieties of plants present. Many plants will not tolerate more than 0.5 to 0.75 g/m^3 (0.5 to 0.75 oz/ 1 000 ft^3). Hough and Mason (1951) have published full lists both of the glasshouse pests which can be controlled with certain dosages and also of the plants which will tolerate these treatments.

Calcium cyanide is particularly useful for a clean-up campaign in empty glasshouses. Under these conditions, dosages of 16 to 32 g/m^3 (16 to 32 oz/l 000 ft^3) of the powder are employed for exposures of not less than 24 hours. The maximum dose is required to eradicate red spiders. As no plant injury is involved in this treatment, a considerable amount of sealing can be done.

Calcium cyanide, which reacts with moisture to give off HCN, must be handled with great care (See Chapter 6).

Methyl bromide Chamber

Methyl bromide is not usually a suitable fumigant for general release in a glasshouse, mainly because it diffuses so rapidly through small leakage holes that it is difficult to maintain the concentrations needed to kill the pests. However, for glasshouses that can be made sufficiently gas tight, it has been used effectively for disinfestation purposes. A chamber for atmospheric fumigation with methyl bromide is of considerable help for dealing with localized infestations on a few plants or for treating stock coming in and going out. Establishments that ship considerable amounts of

material under quarantine often operate their own chambers under the supervision of quarantine officials.

A small chamber of a type described in Chapter 8 with an exhaust vent leading outdoors, can be installed in a well-ventilated part of the premises. Usually such a chamber need not exceed about 6 m^3 (200 ft^3) in capacity.

A handbook giving the tolerances of many plants to methyl bromide has been produced by the U.S. Department of Agriculture (USDA, 1977).

FIELD FUMIGATION UNDER SHEETS

The development of light weight plastic sheets has made it possible to cover sizable areas of land so that volatile chemicals can be contained for sufficient time to effect a treatment either of the soil or of vegetation above the ground. The use of this technique for the control of weeds and of soil-infesting insects and nematodes, is well known. This method has also been used successfully to deal with infestations above ground level.

In California, large beds of strawberry plants infested with cyclamen mites are covered with white polyethylene sheets (tarpaulins), normally 30 x 60 m (100 x 200 ft) in size (Allen, 1957). The tarpaulins are sealed down at the edges with earth or placed under a narrow moat of water. Methyl bromide from cylinders is discharged as "hot gas" under the sheets through plastic hose used for irrigation (soil soakers), so as to give an even distribution of fumigant over the area. Recirculating blowers are also used.

When transparent plastic sheeting is used in full daylight, there is considerable overheating of the plants. This is avoided for the most part by using opaque material. Nevertheless, temperatures under the sheets must be carefully observed by using thermocouples or thermistor thermometers. Exposure is for two to three hours, according to seasonal conditions, with the dosages varying from 24 to 48 g/m^3 (1.5 to 3 lb/ 1 000 ft^3) as the temperatures decrease under the sheets from 30 to 10°C.

In summer, fumigation should be done between crops. Some differences in tolerance to the fumigation are shown by varieties of strawberries, and injury may often be avoided by treating the plants when they are dormant. In the summer, fumigation is best done early in the morning or during the evening. There is evidence that this treatment has a stimulating effect on plant growth. However, it is not recommended that fumigation be done solely for this effect when the mites are not present, because stimulation may sometimes result in small leaves, flowers and fruit (Allen, 1957).

Plastic-coated nylon fumigation sheets were used in a campaign to eradicate over wintering larvae of the oriental fruit moth in the okanagan Valley of British Columbia (Monro, 1958b, c). The insects were lodged on or in the soil and debris in an orchard into which had been dumped some infested waste from a canning factory.

Measures to control the European pine shoot moth by field fumigation with methyl bromide of ornamental pines in commercial nurseries and private properties are described and illustrated in detail by Carolin et al (1962), Klein and Thompson (1962) and Carolin and Coulter (1963).

13. PLANT QUARANTINE TREATMENTS

In plant quarantine work, the object of fumigation is to obtain complete mortality of 81 l stages of the pest against which the treatment is directed. For each prescribed treatment, experimental work has defined certain conditions required to bring about this degree of control. A minimum certification statement of conditions should always contain the dosage, exposure time, and temperature. More exact conditions may be added, such as the minimum concentration x time (c x t) product of fumigant required, or a load factor may be introduced to modify dosage according to the amount of commodity present. Sometimes other factors are stipulated, such as the maintenance of a given humidity in the system during treatment or the amount of vacuum, when applicable.

To be effective, the stipulated conditions must be attained in practice every time the treatment is made.

It may be helpful to review here the more important technical considerations involved in plant quarantine fumigation.

Volatilization of fumigant. A particular treatment calls for a certain dosage or concentration of fumigant for a certain length of time. To attain the desired result, the full concentration must be present from the beginning of the treatment. The beginning of the exposure period can be counted only from the time the fumigant is fully volatilized. Furthermore, if the fumigant evaporates slowly after it is introduced into the system, progressive sorption of the fumigant by the commodity may prevent the attainment of the concentration x time product needed to kill the pest organism in the time allotted.

This consideration is particularly important in treatments of perishable products, such as flowers, growing plants, fruit and vegetables, where the exposures are comparatively short periods of two to four hours. Even when volatile fumigants, such as methyl bromide, are used in treatments at temperatures below 20°C, the fumigants evaporate slowly if they are not artificially heated before or after they enter the chamber. If at all possible, methyl bromide should be introduced as a "hot gas", in the ways already described. If that is not convenient, it should be discharged onto a heated evaporating pan inside the chamber. Ethylene dibromide may be evaporated rapidly in pans placed on hot plates or by means of efficient vaporizing nozzles.

Methyl bromide is recommended for use in certain treatments down to 4°C. Such treatments are likely to fail if the fumigant is not fully volatilized when it is introduced.

Leakage. Leakage from the structure in which treatment is being done may render the treatment ineffective. It is necessary to undertake regular checks of the gas tightness of all chambers, railway cars, trucks or other spaces used for quarantine fumigations. Methods of testing structures for gas tightness are described in Chapters 8 and Il.

Chemical analysis. In practice, the attainment of effective concentration x time products is the only way of ensuring complete control. Therefore, during actual treatments of the quarantined commodities, determinations should be made at regular intervals of time of gas concentrations in different parts of the system to ensure that the necessary concentration x time products are attained.

Test insects. Usually, it is inconvenient to make chemical analyses during every treatment. These analyses may be supplemented by the regular use of test insects. The response of the test insects should be approximately the same as that of the most resistant stage of any pest likely to be encountered. If the reactions of the test insects are related to the results of periodic analyses of the fumigant concentrations, a constant check can be made on the effectiveness of the treatment.

Loading. In the fumigation of produce, such as fresh fruit and vegetables shipped in the normal carrier, the disposition and amount of the load will have to conform to commercial practices at reasonable costs of transportation. It is essential, however, for adequate space to be left at the top and bottom of the load to allow for proper circulation of the fumigant/air mixture. This may usually be ensured by the use of false floors and by the allowance of 30 or 60 cm (1 or 2 ft) of space between the top of the load and the ceiling. The regulations or administrative instructions of quarantine authorities often contain specific requirements for the amount and arrangement of the loads.

Circulation of the fumigant. In short exposures of two to four hours, proper distribution of the fumigant throughout the structure can be attained only by artificial circulation or by thorough premixing of the fumigant/air mixture. Proper conditions of uniform distribution by such means must always be provided in all plant quarantine treatments, including vacuum fumigation.

When tender plants, fruit and vegetables are being fumigated, excessive and continuous air movements may lead to plant injury. With such materials circulation should be gentle and the output of the fans should be adjusted accordingly. Such adjustment, however, must not be made at the expense of the efficiency of the treatment. Destruction of the quarantined pest is the primary and overriding consideration.

Humidity. Plant injury is minimized if high humidity is maintained during treatment without the deposition of free moisture. For practical purposes this means a relative humidity of 75 percent or slightly over. On the other hand, too much water on the fumigated material or condensed on the inside surfaces of the chamber will seriously reduce the efficiency of hydrogen cyanide (HCN) and ethylene dibromide (EDB), and may lead to considerable injury; with the less water-soluble methyl bromide, it may prevent the fumigant from reaching some of the pests.

Effective humidity control systems are available commercially. These employ spray nozzles through which a fine spray of water is driven by compressed air. Close humidity control is ensured by sensitive "humidistats."

Postfumigation treatment of plants. Injury to growing plants may be reduced by treatment appropriate to the fumigant used. Plants to be exposed to methyl bromide and ethylene dibromide should not be watered for 24 hours unless there is danger of wilting. On the other hand, growing plants fumigated with HCN should be gently but thoroughly washed with water to minimize subsequent injury.

FUMIGATION AND COLD STORAGE

For some plant quarantine treatments, fumigation is combined with cold storage to obtain greater control of insects. The San Jose scale, Quadraspidiotus perniciosus (Comstock), and larvae of the coaling moth, Laspreyresia pomonella (1.), are controlled more effectively on apples with methyl bromide treatment followed by storage at -0.5°C than by the use of either of these treatments alone (Moffitt, 1971; Morgan et al 1974, 1975). Also a combination of cold storage for two to four days at 0° to 2°C followed by fumigation with methyl bromide (c x t product 75 mg h/l and 10°C) is effective in eliminating eggs of the cutworm Spodoptera littoralis (Boisd.) from chrysanthemum cuttings (Powell, 1979). Dosage schedules for fumigation plus refrigeration of fruits are given by USDA (1976).

The possibility of causing injury to fruit with methyl bromide or other fumigants should be taken into account whenever these combined treatments are planned. Benschoter (1979) showed that injury to 'Marsh' grapefruit from methyl bromide varies with early, mid and late season fruit and is greater when fumigation is followed by cold storage than when the fruit is held at ambient temperature. Fumigators are encouraged to make test treatments on small quantities of fruit before applying the combined treatments to commercial shipments.

14. EXPERIMENTAL FUMIGATIONS

From time to time, users of fumigants may want to carry out a small scale "test" fumigation to determine the suitability of a treatment. For instance, when a commodity or pest organism, not normally fumigated, requires treatment, a number of questions will arise. The choice of fumigant, conditions of the treatment, including dosage, exposure time and temperature, possible effects on the commodity, possible residues, as well as effectiveness in controlling the pest organism, all need to be considered. Even in well-established fumigations, unexpected problems sometimes arise and tests are needed to determine the cause. Small scale tests are also used to check for resistance of insects to fumigants (see FAO, 1975 for methods for detection and measurement of resistance to fumigants).

In addition to conducting experimental treatments for testing procedures, it is good practice to use insects themselves for test purposes in assessing effectiveness of routine treatments. It is rewarding to spend time on the examination of fumigated insects because the observations and recorded results may also be useful for planning future treatments. The assessment of insect mortality requires great care and good judgement to make reliable decisions as to the effectiveness of a fumigation.

In this chapter, procedures for carrying out small-scale experiments are described. The descriptions refer mainly to the two fumigants methyl bromide and phosphine; however, somewhat similar procedures will apply for other fumigants. The practice of using insects for testing effectiveness of treatments is outlined along with methods of handling and rearing the insects. Also included in this chapter are examples of some of the problems encountered in fumigation treatments, along with discussion on ways to avoid these problems.

EXPERIMENTAL TREATMENT

Small-scale tests are carried out in specially constructed small fumigation chambers or other small containers that will accommodate the test material and can be made gas tight. Metal containers such as the portable drum fumigator described in Chapter 8, glass desiccators or flasks, may be adapted for such tests. Other equipment and material will consist of apparatus for measuring and transferring small amounts of fumigant, a source of the appropriate fumigant and in some cases equipment and methods for analysing gas concentrations. In addition, test insects are often needed for determining effectiveness of the treatment.

FUMIGATION CHAMBER

The general requirements for the fumigation chamber are similar to those outlined for larger chambers in Chapter 8. Good sealing of the door or cover of the chamber is especially important; if a glass desiccator is used, silicone grease on the ground-glass surfaces between the cover and flange will provide a good seal. In addition, some

means of introducing the gas through a gas tight seal is necessary. Silicone rubber stoppers or septa fitted in the wall of the chamber to allow injection by a gas syringe are satisfactory for this purpose. If ampoules of liquid methyl bromide are used, an ampoule breaker similar to that shown in Figure 27 is required.

A small fan, magnetic stirrer or simply a swinging "punkah" type fan should be provided for stirring the gas mixture in the chamber. If an electric fan is used, the motor should be of the spark-proof type. Fumigation chambers designed for phosphine should not have motors or other equipment containing copper.

Measurement of Volume

The volume of the chamber should be carefully determined so that dosage of fumigant can be calculated with reasonable accuracy. For rectangular or cylindrical chambers, measuring the dimensions may be adequate for determination of volume. For small chambers, such as desiccators or flasks, the volume is best determined by filling with water and measuring the volume of water in a suitable measuring container, e.g. a graduated cylinder.

Gas Syrinnes

For small chambers around 50 to 100 l in size, methyl bromide and phosphine are most easily applied as gases using gas tight syringes. The size of syringe required will be influenced by the volume of the fumigation chamber as well as the fumigant concerned. For example, a 500 ml syringe is likely to be suitable for most tests with methyl bromide using a chamber of 50 1 volume, while a 100 ml syringe would be adequate for the lower concentrations of phosphine that are needed.

FUMIGANT SOURCE

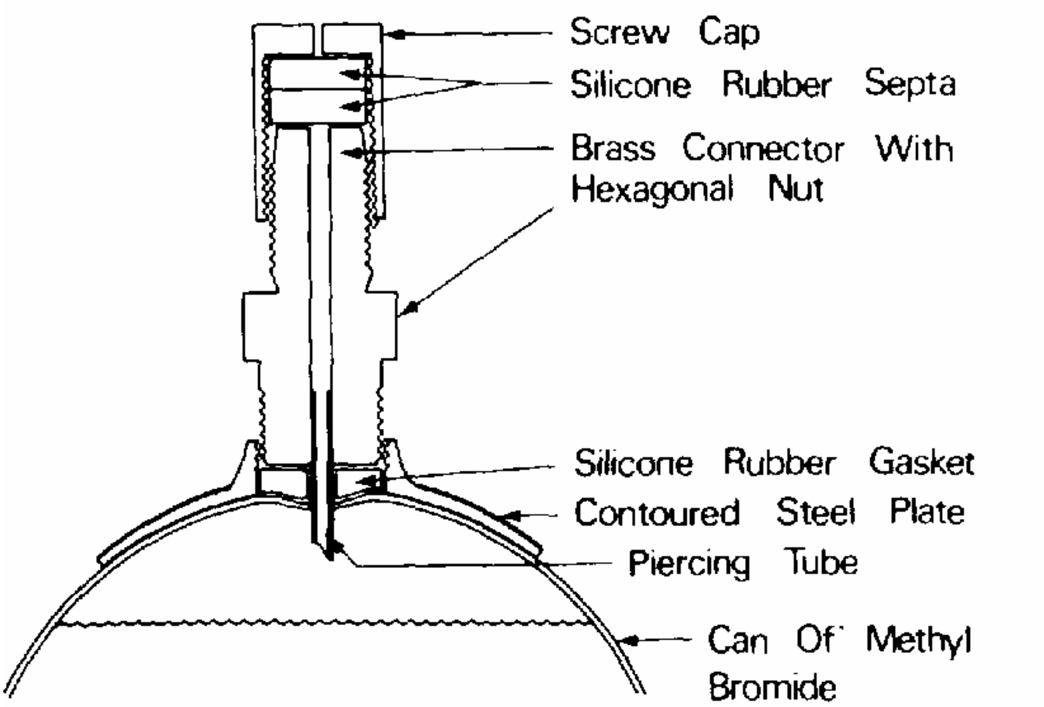
Methyl bromide

Small quantities of this fumigant can be obtained from 454 or 681 9 (1 or 1.5 lb) cans using a can-tapping device specially designed for the purpose (Figure 44). This device consists of a piercing unit made from a 6 mm brass connector fitted with a piercing tube and neoprene gasket at one end and two silicone rubber septa (discs) held in place over the outer end of the connector by a screw cap with a 1 mm hole drilled in the centre. A contoured stainless steel plate for receiving the connector is held firmly to the can by two 90 mm stainless steel clamps.

To pierce the can, the connector is screwed into the threaded hole of the contoured plate until finger tight and then given a quick half turn with a wrench to make the puncture and simultaneously to provide a gas tight seal as the gasket is compressed against the can. Can tapping devices such as this are available from scientific suppliers or they can be made in a machine shop. It should be noted that the use of materials

that do not react with methyl bromide, e.g. neoprene, silicone rubber and brass, is important; aluminium fittings should nut be used.

FIGURE 44. Schematic drawing showing cross-sectional view of the can tapping device.



Samples of the gas are taken by placing the can on its side with the piercing unit pointing upwards, inserting the needle of the syringe through the hole of the brass cap to pierce the septa and allowing the methyl bromide to expand into the syringe as shown in Figure 45. Special syringe-needles, with the hole in the side rather than at the tip, should be used to avoid the problem of blocking by particles of septa during the piercing operation. Best results are obtained when the screw cap is loosened slightly before piercing to allow some expansion of the septa. After the needle is withdrawn, the cap is again tightened to produce a tight seal and prevent escape of methyl bromide. The syringe may be flushed with a small amount of methyl bromide to remove air before the required sample is taken. If the fumigant is taken directly to the fumigation chamber, very little gas will diffuse from the syringe needle. However, shut-off valves for syringes are available or the needle tip may be inserted into a silicone septum to provide a temporary seal.

The fumigation chamber should be located nearby with appropriate ventilation to prevent exposure to the fumigant. Gas masks and suitable detection equipment should be available.

Phosphine

This gas is easily collected from commercial aluminium phosphide pellets immersed in a container of water, as described by Kashi and Bond (1975). A glass tube 27 mm in

diameter drawn out to a narrow neck at one end is filled with water in a graduated cylinder and fitted (under water) with a silicone rubber septum, as shown in figure 46. A pellet is dropped into the cylinder of water and bubbles of phosphine are collected by displacement of the water in the glass tube.

The required quantity of phosphine is withdrawn through the septum with a gas syringe and transferred to the fumigation chamber.

NOTE. It is advisable to flush the syringe with nitrogen before filling with phosphine to avoid the flame that may occur if sufficient oxygen is present. When drawing phosphine into the syringe, the plunger should be pulled slowly to prevent sudden pressure changes.

CALCULATION OF DOSAGE

The volume of undiluted methyl bromide or phosphine gas required to give a prescribed concentration in any small chamber can be easily calculated from the data given in Chapter 2, Table 2. for example, at 25°C the weight of methyl bromide gas that can be contained in 1 m^3 is 3 874.1 9, i.e. 3 874.1 mg in 1 lithe or 3.874 mg in 1 millilitre. To obtain the volume (no. of ml) of methyl bromide required to give 16 mg/l for a 10 1 fumigation chamber, divide the total weight of fumigant required (e.g. 160 mg) by the weight contained in 1 ml (e.g. 3.874 mg) to give 41.3 ml. Similar calculations are made for other temperatures and other fumigants.

FUMIGATION PROCEDURE

After the test material is placed in the fumigation chamber the opening is sealed and the fumigant applied. If test insects are used, care should be taken in selecting representative samples for reliable results.

Experimental fumigations are usually carried out under uniform temperature and humidity conditions, usually 25°C and 77 percent relative humidity, with exposure periods of five hours for methyl bromide and 20 hours for phosphine. However, treatments can be altered to simulate conditions present in commercial operations. At the end of the exposure period the chamber is opened to allow the fumigant to disperse in a fume hood or through properly constructed exhaust ducts.

In conducting experimental fumigations all of the precautions that are applicable to commercial treatments should be observed.

ASSESSMENT OF RESULTS

The type of information derived from a test fumigation will obviously depend on the objective of the treatment; however, much of the information can be obtained soon after the test is made. Effects on commodity, such as corrosion, colour, flavour or odour changes, may be evident immediately after the treatment. In the fumigation of

living plants phytotoxic effects are usually evident within 24 hours. Other effects may be delayed depending on the type of commodity and type of treatment. Gas may continue to desorb from commodities for considerable periods after treatment, making establishment of residue levels difficult. One relatively well-known effect on wheat flour treated with methyl bromide only becomes apparent when a pungent odour is given off from hot bread made from the flour (see Chapter 6).

In assessing the results of test fumigations it may be useful to hold the test material for two to three days, so that due allowance can be made for unexpected effects.

ASSESSMENT OF INSECT MORTALITY

NATURAL INFESTATION

If the insects infesting goods or premises are present in fair numbers, a reliable estimate of the success of a treatment may be made by collecting representatives of the species and stages present. If any of the insects are inside grains, seeds, nuts or other plant material, samples of these should also be taken. If possible, each sample taken from the different positions should weigh not less than 0.5 kg or 1 lb. It is important to collect from as many different positions as possible; small collections and samples from many positions give a better picture than large ones from only a few places. Where bags or packages are concerned, insects and samples should be removed both from the middle and the outside of as many containers as is practicable.

If sieving the infested material is necessary, it may be done at the actual fumigation site, but the insects collected in this way should be handled with care. Insects and samples of the infested material should be placed in small tins or pillboxes which are not absolutely air tight and taken to the office or laboratory as soon as possible. Here they should be transferred to clean jars or bottles containing some of the material they were feeding on. Fresh air must be available to the insects, and cloth, metal or plastic gauze should, therefore, be placed over the top of the new container in a way that will not allow the insects to escape. Petri dishes with the upper cover resting firmly on the lower dish are suitable because they usually do not permit escape and fresh air is able to reach the insects.

Appraisal of Mortality

It is unwise to attempt to appraise the results of the fumigation immediately in terms of insect mortality. With some fumigants, such as methyl bromide and ethylene dibromide, mortality may be delayed. Others, such as hydrogen cyanide (HCN), cause temporary paralysis and the insects may fully recover some time after they are restored to fresh air. It is advisable, therefore, to leave the insects in a warm place (20 to 30°C) overnight before mortality counts are made and before definite conclusions are reached as to the success of the treatment. Some insects feign death. If gentle heat radiating from a 40- or 60-watt lamp is applied to the insects, the living individuals normally resume active movements within a short time.

Samples of the infested material, which may contain immature stages of the pests, (e.g. see Section 'Toxicity' under phosphine in Chapter 6) should be kept in 1 litre (2 pint) glass jars covered with 20 mesh to the inch (2.5 cm) screening. This material should be kept, if possible, in a warm room (20 to 30°C) at not less than 70 percent relative humidity and examined or screened periodically to watch for emergence of adults.

TEST INSECTS

Some thought and care must be given to the way in which test insects are used, otherwise conclusions based on their mortality may be misleading. For instance, if the insects are brought from a warm room and exposed in a treatment conducted at a much lower temperature, they might, with certain fumigants, be more likely to succumb than if they have been conditioned to the temperature of the fumigation for several hours or days before it begins. This and related aspects of insect reaction to fumigants were discussed in Chapter 2.

As a general rule, test insects should be exposed as adults, unless special information is needed on immature stages. The insects should not be placed in bare cages or other containers used for holding them during exposure; they should be put in with some of the normal food used in the rearing culture. The containers should not be jammed full with either food or insects. A container three quarters full of food with about 30 to 50 insects is a good arrangement. A better interpretation of results is obtained by dispersing the available test insect population in many places in small numbers rather than by concentrating large numbers in only a few stations.

Test Capes

Cages or containers may be improvised from available materials or bought from dealers. If the containers are exposed in the free space of a fumigation system or placed between packages or bays, tins with capacity of 30 to 60 ml (1 to 2 oz) may be used. At both top and bottom of the can a hole 2 cm (0.75 in) in diameter should be punctured and the hole closed on the inside by fine mesh or plastic screening, which should be soldered or strongly glued to the metal. The mesh of the screening will depend on the insects being used; 20 mesh to the inch (2.5 cm) is suitable far most purposes and is recommended for the two species mentioned below. Experience will show the best way to use available materials. Some insects will bore through cloth or plastic screening.

Other types of cages may be made from cylinders of metal or plastic gauze, a good size being 12 x 6 cm (5 x 2.5 in). The seam may be soldered or some of the wire wound in a spiral around the gauze cylinder while it is rolled firmly on a metal rod (Brown, 1959). The ends of the cylinder may be plugged with corks or cotton batting (some species may become entangled in the cotton).

As mentioned in Chapter 6, phosphine reacts strongly with some metals, more especially copper. Copper, or copper containing alloys, should not be used in the construction of test cages to be used with this fumigant. Stainless steel is suitable if it is low in copper content. Generally, it is better to use plastic cages and screening for test purposes when working with phosphine.

Metal Probes

For the purpose of testing the reactions of insects inside a closely packed commodity, metal probes, available commercially, may be used. These have narrow, cylindrical pointed heads, which may be thrust deep into dense materials. These heads are small chambers 5 or 8 cm (2 or 3 in) long with narrow slits on three or four sides to allow the fumigant to diffuse in. The heads are threaded to the main stem of the probe so that the insects with their culture material may be put in and taken out. Probes may also be specially made in a laboratory or industrial machine shop.

Interpretation of Results

The same considerations already discussed for the handling of insects infesting the material, and for the interpretation of mortalities observed, apply also to test insects. As suggested, judgement must be exercised in assessing the results obtained. Until an observer has had considerable experience in using test insects to indicate the success or failure of commercial fumigations, he must be especially wary of undue optimism based on a few favourable results.

Species Used

For general fumigation work, the granary weevil, Sitophilus qranarius (or other species of Sitophilus) and the confused flour beetle, Tribolium confusum, are easily reared and are suitable to use for test purposes. Also, as Table 16 shows, they vary in their response to different fumigants. For instance, S. qranarius is more resistant to HCN and chloropicrin and T. confusum is more resistant to CS_2, ethylene oxide and methyl bromide. If both insect species are available, it is advisable to test the one that is more resistant to the particular fumigant or mixture of fumigants being used.

TABLE 16. CONCENTRATION x TIME PRODUCTS* OF CERTAIN FUMIGANTS REQUIRED FOR THE CONTROL OF VARIOUS SPECIES OF INSECTS

Fumigant	*Oryzaephilus surinamensis* Adults **LD95 6 h 21°C	*Rhyzopertha dominica* Adults LD95 6 h 21°C	*Sitophilus granarius* Adults LD99 5 h 25°C	*Sitophilus oryzae* Adults LD95 6 h 21°C	*Tenebroides mauritanicus* Larvae LD99 5 h 25°C	*Tribolium confusum* Adults LD99 5 h 25°C	*Tribolium castaneum* Adults LD90 6 h 24°C	*Trogoderma granarium* Larvae LD95 6 h 21°C
Acrylonitrile	[4]8.4	[4]8.4	[1]11.0	[4]10.8	[1]40.0	[1]19.5	---	[5]48.0
Carbon disulphide	[4]408.0	[4]294.0	[1]325.0	[4]300.0	[1]828.0	[1]560.0	---	[5]696.0
Carbon tetrachloride	---	---	[10]4 495.0	[9]2 220.0	[1]2 400.0 (LD50)	[10]2 025.0	[11]600.0	---
Chloropicrin	[4]19.2	[4]15.6	[1]150.0	[4]23.4	[1]56.0	[1]57.5	[11]14.0	[5]96.0
Ethylene dibromide	[4]19.2	[4]37.2	[1]34.5	[4]60.0	[1]125.0	[1]31.0	[7]22.0 (LD95) 4 h 27°C	[5]80.0
Ethylene dichloride	[4]462.0	[4]636.0	[10]1 230.0	[4]738.0	[1]1 728.0	[10]365.0	[11]462.0	[5]2 080.5
Ethylene oxide	[4]60.0	[4]69.6	[1]36.0	[4]62.0	[1]175.0	[1]127.5	[3]135.0 (LD99) 5 h 25°C	[5]176.0
Hydrogen cyanide (HCN)	[4]7.2	[4]15.6	[1]67.5	[3]60.0 (LD99) 5 h 25°C	[1]66.5	[1]5.5	[7]2.4 (LD95) 4 h 27°C	[5]26.4
Methyl bromide	[4]40.8	[4]33.0	[1]28.0	[2]30.0 (LD99.9)	[1]115.0	[1]64.0	[7]62 0 (LD95) 4 h 27°C	[5]136.0
Phosphine (24 hr exposure 27°C)	[8]0.96 (LD99)	[8]0.6 (LD99)	[8]1.01	[8]0.36 (LD99)	[1]5.0 approx.	[8]0.48	[11]11.5	[6]331.0 100% mort. 72 h 21°C
Sulphuryl fluoride	---	---	[1]17.5	---	[1]81.5	[1]55.0	---	---

*In terms of milligramme hours per litre - **LD = Lethal dose - [1]Bond and Monro (1961) - [2]Brown (1959) - [3]Busvine (1938) - [4]Lindgren et al (1954) - [5]Lindgren et al (1955) - [6]Lindgren et al (1958) - [7]Lindgren and Vincent (1965) - [8]Lindgren et al (1966) - [9]Majumder (1962) - [10]Shepard et al (1937) - [11]Bang and Telford (1966).

Rearing Test Insects

For general use, the two species mentioned are best reared at 25°C and 70 percent relative humidity in an incubator box. If an incubator is not available, rearing may be done in an ordinary office room in which the temperature does not fall below 20°C. If necessary, moist conditions can be provided by placing the culture bottles in a box or small cupboard with a small fan blowing across a flat pan of water. Other methods of maintaining a reasonable humidity may be devised. The humidity is important because Tribolium, especially, does not rear well under dry conditions.

The insects are reared in screw-top glass jars of 1 litre (2 pint) capacity. The glass lids are replaced by discs of plastic or metal screening of not more than 20 mesh to the in (2.5 cm), which are fitted tightly by means of the screw tops after the insects are introduced.

Granary weevil. Place 350 9 (0.75 lb) of soft wheat in the glass jars. Introduce from 100 to 250 active granary weevils (100 adult weevils occupy approximately 1 ml in a measuring cylinder) and leave them on the wheat for two to three days. If only small numbers are available, they should be left for a longer time; and it may take several generations before populations adequate for test purposes are built up. After five or six weeks, weevils will start to emerge. At this point it is a good idea to sieve and transfer the insects to fresh jars of wheat once a week. The date of transfer is marked on the fresh bottle. Regular weekly transfers provide for the starting of new cultures. The weevils are best used for test between two to four weeks after emergence from the kernels.

The granary weevil is able to survive for over a month at temperatures between 0 and 5°C and is tolerant to temperatures as low as -10°C for about two weeks. It is, therefore, suited for use as a test insect in fumigations at low temperatures.

Confused flour beetle. This insect is reared on whole wheat flour. The culture jar or bottle should be only about half full of flour. On the flour, place between 100 and 200 adults, which should be taken off by sieving through a 20-mesh screen after a week and placed in another jar. The new generation of 1 000 to 2 000 adults will begin to appear after about one month and these insects may be used for test purposes two to four weeks after emergence.

Adults of T. confusum should not be allowed to become too crowded in the culture bottles, because the insects emit a vapour which may be self toxic. Overcrowding is indicated when the flour turns pink from reaction with this yes. In view of the fact that autointoxication is possible with the confused flour beetle, great care must be taken to make sure that test cages are well ventilated when in transit to and from the fumigation site.

The confused flour beetle is sensitive to low temperatures and is best used at temperatures above 10°C.

Other test species. Other species of insects, more particularly species of beetles which are fairly easily reared, are suitable as test insects. The Khapra beetle is recommended by Brown (1959) because it is resistant to methyl bromide. This insect should be used only in countries where the species is endemic. Spider beetles (Ptinus spp.) are useful for tests at temperatures below 10°C, but they are not as easily reared as the species mentioned above.

Information on the rearing and handling of many insect species suitable for use as test insects is given by Campbell and Moulton (1943).

FUMIGATION FAILURES

The effectiveness of a fumigation depends on many factors - the properties of the fumigant, the gas tightness of the chamber, the nature of the commodity, the condition of the environment and the type and condition of the target organism all have direct effects on the treatment. Occasionally, well established treatments do not give the expected control or other unexpected effects may occur; very often the reasons for such results are not immediately apparent.

Throughout this manual many potential problems with the fumigants themselves or with the fumigation procedure have been referred to. Most of these problems can be avoided or overcome by having a good working knowledge of the fumigants and by continually exercising care in their use. Some of the usual reasons for failures include:

- inappropriate choice of fumigant;

- improper application;

- uneven gas distribution;

- poor penetration of goods;

- loss of fumigant through leakage;

- temperature variations, especially low temperatures;

- excessive sorption by materials;

- insect resistance.

A fumigation treatment may be considered as a failure if the pest organism is not controlled or the commodity is damaged.

LACK OF CONTROL

Any insects that survive fumigation do so because they have not absorbed enough of the toxicant for it to be effective. Dosage schedules are designed to cope with most variability's, such as species, stage or condition of the insects, and they are made for a range of temperature conditions. Difficulties usually arise from unobserved or unusual conditions that prevent the fumigant from reaching the insects. Loss of gas through leakage or absorption can be a major reason for lack of kill and poor penetration into a commodity can be another.

Most problems concerning loss of gas can be avoided by proper preparation for the treatment and analysis of gas concentrations at appropriate locations during the exposure period. Information on gas concentrations gives the fumigator a high degree of control over the operation; it can give a good indication of gas dispersal, maximum levels attained, penetration into materials or loss from the space. Problems can usually be overcome by extending the period of fan circulation, by adding more fumigant or by extending exposure time.

Temperatures within a commodity or at different locations in a structure can vary greatly so that insects in areas of lower temperature may survive. Ranges of 10 – 20°C or more in commodity and free space con occur, particularly in structures exposed to strong sunlight. It should be noted that at temperatures around freezing the effectiveness of a fumigant is quite variable and may not give control (see Chapter 2). Since fumigant effectiveness is closely related to temperature, the dosage must be adjusted to the lowest temperature for complete control.

Insect resistance (see Chapter 2) is a matter of great concern to those using fumigants because of the small number of fumigants available and because of the lack of effective alternatives. Any indication of resistance to fumigants should be thoroughly investigated. If control procedures become ineffective when conducted according to recommendations, a careful check should be made for resistant insects. The FAO(1975) method for detection and measurement of resistance can be used. If resistant insects are found, measures should be taken to eradicate the population completely and thus prevent dispersal to other areas.

DAMAGE TO THE COMMODITY

Although recommended treatments are designed to kill pest organisms without any effect on the commodity, unexpected injury to plants or damage to other materials does occasionally occur. Many of the different effects that fumigants can have on materials are given in Chapter 6. Information on the tolerance of various plants and plant materials are also given in the dosage schedules.

Some of the types of damage that should be guarded against include corrosion, fire or explosion and changes in odour or taste.

Corrosive effects. Damage may result if methyl bromide comes in contact with flame or hot wires to form the corrosive hydrobromic acid. Phosphine can damage electrical equipment with copper wires, particularly in conditions of high humidity.

Odour and taste effects. Methyl bromide occasionally reacts with flour to produce offensive odours during baking or in hot loaves of bread. A list of other materials that are adversely affected by methyl bromide is given in Chapter 6.

Fire and explosion. Although treatments are always designed to avoid any condition that will produce fire or explosion, accidents do occur at times. Containers of phosphine fumigant may occasionally flash when first opened due to release of accumulated phosphine gas. For this reason, they should always be opened out of doors away from any flammable material. Fires have occurred on grain ships when phosphine producing formulations that had been laid on the surface of the grain cargo shifted during the voyage to accumulate in one corner of the hold. Such formulations should always be used so as to avoid any possibility of high concentrations of phosphine accumulating in confined spaces.

FUMIGATION AND DUST EXPLOSIONS

Concern over a possible connection between the presence of fumigant in grain and grain dust explosions has been expressed; however, it must be pointed out that the matter is uncertain at the present time. Some tests have given evidence to suggest that there may be significant interactions between fumigant vapours and explosive dusts; tests with a mixture of 80 percent carbon tetrachloride and 20 percent carbon disulphide, which by itself is non-flammable, were found to lower the explosive concentration of commercial flour dust appreciably (Atallah, 1979). However, another investigation with three fumigant mixtures, containing carbon tetrachloride and ethylene dichloride or carbon disulphide, showed that there was no increase in the severity of grain dust explosions and in some cases the vapours actually suppressed the explosion (Tait et al, 1980).

The uncertainty about any connection between fumigation and dust explosions will remain until further information is available. However, due precautions against creating a hazardous combination may be warranted, particularly with fumigants that have relatively low flammability limits.

15. TRAINING IN FUMIGATION

The effective and safe use of fumigants is dependent on a good knowledge of both the chemicals that are used and the procedures employed in fumigating. Present standards and restrictions on the use of pesticide chemicals also require the fumigator to know many things that were disregarded in the past. Personnel using fumigants should have practical knowledge of the pests they are dealing with, they should know the hazards involved in using fumigants and they should be familiar with methods of detection and analysis. Also, they should know safety and first aid procedures and have some knowledge of official regulations governing the use of these materials.

Many national or local governments require that fumigators be trained and licensed before they are permitted to apply fumigants. A working knowledge of the technical and business aspects of pest control can be best achieved by a period of study and training. On-the-job experience is important, but this approach alone can lead to mistakes and offers fewer opportunities for career advancement (Osmun, 1976). Training courses should include instruction on the basic principles of fumigation and pest control, practical demonstrations on procedures and a period of apprenticeship with an experienced fumigator. Competence for certification is determined on the basis of written examinations and performance testing. Refresher courses are given in some countries to ensure that high standards of competence are maintained and that applicators become familiar with new developments as they take place.

From the viewpoint of the truly professional fumigator, every applicator should want to become certified, as this is the only way he is likely to be exposed to sufficient training to become professional. For the employer, the value of good training for his employees will be evident in their competence and ability to carry out the operations in an effective, safe and professional manner.

The information given in this book can serve as the basis for a course of instruction in fumigation. Chapters dealing with principles of fumigation, properties of fumigants, methods of analysis, safety precautions and protective devices are particularly important. A comprehensive course on fumigation would include the following subjects:

1. General introduction to the principles of pest control, including a brief account of methods of food storage and preservation, infestation and destruction of food and other commodities by pest organisms, methods of prevention and control of infestations, integrated pest management programmes.

2. Principles of fumigation

a. Definition of a fumigant; choice of fumigant; vaporization of fumigants; latent heat of vaporization; law of diffusion; specific gravity and distribution; mechanical aids to diffusion, sorption and desorption; chemical reactions; residues.

b. Dosage and concentration; calculations for conversion of concentration values; concentration x time (c x t) products.

c. Toxicity to insects; bioassay techniques; comparative toxicity of various fumigants; effect of temperature, humidity and other gases on toxicity; fluctuations in insect susceptibility and effects of nutrition, species, stage and climatic changes on these; resistance testing.

3. Methods of detection and analysis - chemical methods, instrumental analysis, types of instruments available for field and laboratory use, instruments used for health safety.

4. Safety precautions and protective devices.

a. Threshold limit values; hazards; acute and chronic toxicity; detection of fumigants in the atmosphere; symptoms of poisoning; first aid measures and medical treatment.

b. General precautions in handling fumigants - in preliminary preparations; during application; during treatment; post treatment; protective clothing; respirators - self contained, air-line and canister type.

5. Properties of individual fumigants

a. General characteristics, including corrosive nature and in flammability; toxicity to insects; effect on seeds, bulbs, growing plants, dormant plants (phototoxicity) and plant products including fresh fruit and vegetables, cereal products; effect on animal products; residues.

b. Detection of vapours; field analysis; methods of application; methods of sealing structures; methods of aeration.

c. Safety precautions - specific health hazards, methods of detection for health safety, symptoms of poisoning, respiratory and general body protection, first aid, medical treatment.

6. Biology, life history and identification of insects and other pest organisms. This is particularly important in insect control since control measures may vary with different species.

PRACTICAL TRAINING

Demonstrations plus active individual participation in performing the various procedures involved in fumigation are considered to be essential parts of any course of instruction. The practical training should demonstrate with step-by-step directions how to carry out various procedures. Similarly, it should emphasize the importance of

systematic planning and conduct of every stage of a fumigation operation from initial planning to final clearance of fumigant. Planning should include the following steps:

1. Preliminary inspection of facilities to be fumigated.

2. Arrangements with officials and personnel, plus notification of appropriate authorities - fire, police departments, etc.

3. Materials required for the fumigation.

4. Duties to be performed by each individual of the fumigation crew.

5. Preparation of the facility to be treated.

6. Pre-application procedures.

7. Fumigant application and operations to be performed during the treatment (surveillance for gas leaks, analysis of concentrations).

8. Aeration and post-fumigation procedures.

A check list that gives a record of all equipment required and all duties to be performed should be made.

Demonstrations

Practical demonstrations of the following types may be considered.

1. Methods of storage; handling fumigants - solids, liquids, gases; proper disposal of used containers and end products remaining after a treatment.

2. Demonstration of equipment used for detection and analysis, e.g. halide leak detector, thermal conductivity analyses, glass detector tubes, interference refractometer plus infra-red analyses and portable gas chromatographs, if available.

3. Proper care and use of protective devices; respirators - self contained, air-line and canister types; safety blouses; first aid procedures.

4. Bioassay - treatment of test insects with fumigant; assessment of mortality; determination of LD(50) and LD(99).

5. Stack fumigation to include step-by-step planning of the various procedures involved in a fumigation - choice of fumigant; use of test insects; covering and sealing the stack with a gas-proof sheet; determination of volume of space to be fumigated and quantity of fumigant required; application of fumigant; analysis of fumigant; calculation of c x t product; safety measures; aeration. Factors such as sorption and

desorption, effects of temperature and other atmospheric conditions should also be noted.

6. Other demonstrations and projects requiring active student participation can be designed to fulfil individual needs, depending on the nature of fumigation operations that are anticipated. For large-scale fumigations, such as warehouses, mills or ships, the importance of systematic planning and conduct of all aspects of the treatment should be emphasized.

APPRENTICESHIP

A period of on-the-job training with an experienced fumigator will enable the student to observe first hand many of the principles and practices described above. A period of at least six months, hut preferably one year, should provide enough experience to allow the new fumigator to use fumigants effectively and safely and to adapt his treatments to the varying situations that he may encounter.

FUMIGATION SCHEDULES

The treatments listed in these schedules have been successfully applied in practice. Nevertheless, they are given here for the purpose of reference only. Modifications may have to be made, after preliminary trials, to suit local conditions. Although the schedules represent a wide range of treatments, they do not include all possible applications. Rather, an attempt has been made to select representative schedules from different parts of the world.

Instructions for application of fumigants are usually given on the label affixed to the container in which the fumigant is supplied. In some countries the information given on these labels, including dosage recommendations, is carefully controlled by legislation and, therefore, the use of the fumigant should conform to these national requirements.

A. Bulk fumigation of grain in upright storage.

B. Bulk fumigator of grain in flat storage.

C. List of plants that have sustained injury from fumigation with methyl bromide.

D. Methyl bromide fumigation of actively growing plants.

E. Methyl bromide fumigation of foliated, dormant plants.

F. Methyl bromide fumigation of non-foliated, dormant plant material.

G. Methyl bromide fumigation of orchids.

H. Methyl bromide fumigation of fresh fruit at atmospheric pressure.

I. Methyl bromide fumigation of fresh vegetables.

J. Ethylene dibromide fumigation of fresh fruit.

K. Ethylene dibromide fumigation of fresh vegetables.

L. HCN fumigation of fresh fruit.

M. HNC fumigation of dormant nursery stock.

N. Fumigation of flower bulbs and corms.

O. Methyl bromide fumigation of cut flowers and greenery.

P. Atmospheric and vacuum fumigation for the control of pests infesting packaged plant products.

Q. Fumigation of mills, empty structures, and tobacco warehouses.

R. Local (spot) fumigants for mills.

S. Fumigation of seeds.

T. Fumigation for controlling rodents and other mammalian pests, snakes, birds, snails, ants' nests, wasps and termites.

A valuable source of information for plant quarantine treatments is the Plant Protection and Quarantine Treatment Manual (USDA, 1976 with updated inserts) issued by the Plant Quarantine Division, United States Agricultural Research Service, Washington 25, D.C., which is kept up to date by periodic revisions.

GUIDE TO SCHEDULES A AND B

INSECT SPECIES

Schedules are for all stages of both internal and external grain feeders.

Exception. With fumigants containing bromides or chlorides (halogenated hydrocarbons and chloropicrin) and with ethylene oxide, double the dosage for any species of Trogoderma (Dermestid beetle genus, which includes T.qranarium, the Khapra beetle) and for the cadelle, Tenebroides mauritanicus, should be applied.

STRUCTURES

Schedules given are for concrete and metal structures. For **wooden bins, only direct mixing and surface application** are applicable, and for these the dosages should be **doubled.**

CARRIERS

Treatments of bulk grain may be made in carriers such as closed railway freight cars and road trucks. With due allowance for the tightness of these vehicles, dosages and exposures may be based on the recommendations in Schedule B. Liquid or solid-type fumigants may also be applied to grain in open vehicles if the grain is covered with gas-proof sheets after application of the fumigant (see Chapter 10).

ABBREVIATIONS

Fumigant mixtures by percentage composition (see Chapter 7)

Example. EDC75:CT25 means a mixture of 3 parts ethylene dichloride, 1 part carbon tetrachloride. **All proportions are by volume unless other wise stated.**

DOSAGES

Dosages in Column 2 are for major cereals, including shelled maize, unless otherwise stated under "Remarks." For Grain sorghum multiply rate given by 1.5 to 2 times. Dosages are based on full bins or storages. Special allowance must be made for partially filled structures.

MIXTURES

The fumigant mixtures given are representative of many combinations marketed. Other ingredients include chloroform, methyl allyl chloride and trichloroethylene. These are usually mixed with the more toxic ingredients: carbon disulphide, chloropicrin, ethylene dibromide or ethylene dichloride. Select the dosage from a similar mixture in this schedule containing the same more toxic ingredient.

TEMPERATURES

Schedules are given for grain temperatures of 21 to 25°C. For other temperature ranges apply factors as follows:

10 TO 15°C	Multiply dosage by 1.5
16 TO 20°C	Multiply dosage by 1.25
25°C AND OVER	Use 0.75 of dosage given

It is inadvisable to attempt fumigation when the grain temperature is below 10°C. Hydrogen cyanide (HCN) or calcium cyanide should not be applied at grain temperatures below 15°C.

Fahrenheit equivalents can be obtained by reference to the Table in Appendix 2.

DOCKAGE

If there is dockage present, or the grain is "tough," add 25 percent to dosage already calculated.

SEED GRAIN

Where grain is to be used for seed, do not fumigate if moisture content is above 12 percent. Also, exposure periods for seed should not exceed 24 hours with fumigants containing methyl bromide or chloropicrin or 72 hours with any other fumigant. Do not use ethylene or propylene oxides (see Chapter 6 for effects of individual fumigants on seeds).

FORCED DISTRIBUTION

As stated in Chapter 10, forced distribution may be used without modifying existing aeration systems. Usually dosages given in the schedules for recirculation should be multiplied by 1.5.

HOT SPOTS

Treatments of localized areas of infestation (hot spots) in a L, rain mass are discussed in Chapter 10. A good material for this type of treatment is the mixture EDB 70: methyl bromide 30, by weight, applied at I kg/ 36 m^3 (36 oz/1,000 bu) of grain. The fumigant is applied through tubes or metal pipes into the region of the hot spot.

FURTHER REFERENCES

For more detailed information on schedules for grain fumigation, consult USDA, (1982). Comprehensive information on fumigant residues is given by Lindgren et al (1968).

SCHEDULE A. BULK FUMIGATION OF GRAIN IN UPRIGHT STORAGE

FUMIGANT	DOSAGE PER M^3	DOSAGE PER 1000 BUSHELS[1]	MINIMUM EXPOSURE (DAYS)	REMARKS
Direct mixing				
Calcium cyanide	155 g	12 lb	7	May stain white maize and polished rice
Chloropicrin	26 g	2 lb	1	Should be removed by aeration after 24 hours
Mixture EDC75:CT25	0.44 1	4 gal	3	For maize x 1.5
Mixture $CS_2$16:CT84	0.27 1	2.5 gal	3	Mixture may contain 1 to 2 % SO(2)
Mixture EDB7:EDC30:CT63	0.21 1	2 gal	3	For maize x 1.5
Phosphine	1-2 g	35-70 g	4	7 days at 10-15°C 6 days at 16-20°C 5 days at 21-25°C 4 days at 26°C or above
Surface application (gravity distribution)				
Mixture EDC75:CT25	0.44 1	4 gal	7	For maize x 1.5
Mixture $CS_2$16:CT84	0.33 1	3 gal	7	For maize x 1.5
Mixture EDB7:EDC30:CT63	0.27 1	2.5 gal	7	For maize x 1.5
Carbon tetrachloride	0.55 1	5 gal	14	More often used in combination
Recirculation				
Methyl bromide	26 2	2 lb	1	Should be removed by aeration after 24 hours
Hydrogen cyanide (HCN)	39 g	3 lb	1	Grain should be thoroughly aerated before removal
Mixture Chloropicrin 85: Methyl chloride 15	26 g	2 lb	1	Should be removed by aeration after 24 hours
Mixture ETO10:$CO_2$90	386 g	30 lb	1	Do not use on seed
Mixture CH_3Br70:EDB30	13 g	1 lb	1	Should be removed by aeration after 24 hours

[1]Bushels and gallons are in U.S. volumetric measurements. All dosages, unless otherwise stated, are given for a grain temperature range of 21 to 25 °C(See Chapter 7 for other fumigant mixtures similar to those listed above).

SCHEDULE B. BULK FUMIGATION OF GRAIN IN FLAT STORAGE

FUMIGANT	DOSAGE PER M^3	DOSAGE PER 1000 BUSHELS[1]	MINIMUM EXPOSURE (DAYS)	REMARKS
Application by probe				
Phosphine 1 to 2 g		35–70 g	4	7 days at 10–15°C 6 days at 16–20°C 5 days at 21–25°C 4 days at 26°C or above
Surface application (gravity distribution)				
Mixture EDC75:CT25	0.49 1	4.5 gal	7	For maize x 1.5
Mixture $CS_2$16:CT84	0.55 1	5 gal	7	For maize x 1.5
Mixture EDB7:EDC30:CT63	0.44 1	4 gal	3	For maize x 1.5
Methyl bromide	32.0 g	2.5 lb	1	Applied under gas tight sheet in South Africa. Must be removed by aeration after 24 hours
Recirculation				
Methyl bromide	38.6 g	3 lb	1	Should be removed by aeration after 24 hours
HCN	38.6 g	3 lb	1	Should be thoroughly aerated before grain is moved.
Mixture Chloropicrin 85: Methyl chloride 15	38.6 g	3 lb	1	Should be removed by aeration after 24 hours
Mixture CH_3Br70:EDB30	19.2 g	1.5 lb	1	Should be removed by aeration after 24 hours

[1]Bushels and gallons are in U.S. volumetric measurements. All dosages, unless otherwise stated, are given for a grain temperature range of 21 to 25 °C, unless otherwise stated.

SCHEDULE C. LIST OF PLANTS WHICH HAVE SUSTAINED INJURY FROM FUMIGATION WITH METHYL BROMIDE

As explained in the text, many species and varieties of plants are tolerant to methyl bromide, and those which have been injured are a small percentage of the total number tested.

Some plants may show temporary injury, such as leaf burn, leaf fall or loss of bloom, followed by complete recovery. Others are either killed outright or are so seriously injured that fumigation is out of the question. Therefore, the response is divided into these two categories.

The plants listed as having been injured while non-dormant will generally be tolerant when dormant. On the other hand, plants injured when dormant would be even more susceptible to injury when actively growing. The references (a to j) given after each plant variety are listed at the end of this schedule. When the reference after an item is omitted, it will be found immediately below, with the last species or variety of the same genus.

For the most part, the plants listed here have sustained the injury in fumigation at atmospheric pressure. Plants are usually much more susceptible to injury in vacuum fumigation; for that reason it is recommended only under special circumstances, as in parts of Schedules F and G.

Further information on a wide variety of plant species is given in the "Handbook of Plant Tolerances to Methyl Bromide", USDA (1977).

A. NONDORMANT GROWING PLANTS

In this group of plants, injury has been observed following treatment at rates shown in Schedule D.

1. PLANTS SHOWING TEMPORARY INJURY AFTER TREATMENT, FOLLOWED BY COMPLETE RECOVERY

Acacia appears susceptible to temporary injury. The following species showed leaf fall, then recovery (c,d):
A. baileyana, A. decurrens, A. melanoxylon, A. verticillata
Aglaonema sinensis (a)
Aloe spp. (e)
Amphicome arguta (e) (see Incarvillea)
Araucaria excelsa (Norfolk Island Pine) (a)
Azara microphylla (c,d)
Banksia spp. (c)
Begonia fuchsioides (h)
Berberis spp. uninjured, except:

B. gagnepainii
B. julianae, which should be fumigated when dormant (e)
Bouvardia var. Giant Pink (a)
Bouvardia humboldtii (a)
Bryophyllum spp. uninjured, except 3 species (e):
B. aliciae, mature leaves lost.
B. miniatum, mature leaves lost
B. tubiflorum, lower leaves burned
Cactus spp. found tolerant by (a) and (e), but fumigation not recommended by (c)
Calathea vandenheckei (a)
Capsicum frutescens (red pepper) (c,d)
Cinchona spp. are tolerant, except:
C. pubescens
C. officinalis, showed slight tip burn (e)
Clerodendrum speciosissimum (glory bower) (c, d)
Cotoneaster franchetii (b)
Cotyledon spp., occasional tip burn only (e)
Crassula arborescens (a)
Cytisus racemosus (broom). Other species tolerant (c,d)
Elaeagnus pungens (c,d)
Erica spp. (heath) (d)
Erythrina crysta-gallii (cockspur) (c,d)
Eupatorium ligustrinum, tip burn on very youngest leaf (e)
Euphorbia fulgens (scarlet plume), probably subject to leaf drop (a)
Fatsia japonica (c,d)
Ficus pandurata (fig) (d,e)
Fuchsia spp. (c,d,i)
Gardenia veitchii. Other species tolerant (a)
Genista monosperma (broom) (c,d) -
Geranium spp. (c,d)
Hibiscus spp. (c,d)
Hoheria spp. (c)
Howea forsteriana (a)
Hoya carnosa (wax plant) (c,d)
Incarvillea (e)
Jacaranda spp. (e)
Kitchingia (Kalanchoe) peltala (e)
Lantana spp. (lion's ear) (c,d)
Leonotis leonurus (c,d)
Leptospermum. All species (c)
Luculia. All species (c)
Maranta spp. (c,d)
Myrtus communis (myrtle) (c,d)
Nephthytis afzelii
Nephthytis liberica (a)

Nerium oleander (c,d)
Nothofagus. All species (c)
Oncoba routledgei (e)
Osmanthus ilicifolius (aquifolium) (c,d)
Pandanus veitchii (screw pine) (c,d)
Philodendron cordatum, P. dublum (a)
Pittosporum spp. (c,d,e)
Pothos wilcoxi (f)
Psidium guajava (guava) (c,d,e)
Solanum pseudocapsicum (Jerusalem cherry). Many other species not injured (c,d,e)
Spartium juncoum (Spanish broom) (c,d,e)
Spirea reevesiana (b)
Theobroma purpureum (e)
Viburnum macrophyllum
Viburnum odoratissimum (f). Many other species not injured (a)
Vitex lucens-puriri (c)

2. PLANTS KILLED OUTRIGHT OR SERIOUSLY INJURED

Abelia grandiflora (c,d)
Adiantum (maidenhair fern) (c,d)
Allamanda johnsoni (j)
Areca palm (c,d)
Asplenium nidus (bird's nest fern) (c,d)
Aster fruiticosus (c,d). Many other species tolerant
Begonia semperflorens (c , d)
Begonia tuberhybrida (c , d)
Billbergia alberti, B. nutans (a)
Camellia spp. seem to be tolerant, except C. thee, which has been seriously injured (b)
Cardiospermum integerrimum (heart seed) (e)
Celosia cristata (c,d)
Chamaecyparis spp. (false cypress) (c,d,f)
Chryeanthemum spp. may be fumigated when fully dormant (c,d,i)
Coleus blumei (c,d)
Cuphea hyssopifolia (c,d)
Cupressus arizonica, C. macrocarpa showed initial injury but soon recovered (c,d)
Cupressus sempervirens (cypress) intolerant
Dracacna warneckii (j)
Euphorbia (c,d)
Fremontia (Fremontodendron) californica (flannel bush) (c , d)
Griselinia littoralis (c,d)
Kalanchoe synsepala (e). Many other species tolerant
Lavandula pedunculata (lavender) (c,d)
Leucospermum. All species (c)
Monstera deliciosa (a)

Musa spp. (banana) (c,d)
Pelargonium hortorum (i)
Poinsettia (Euphorbia) spp. (c, d)
Pyracantha formosana (firethorn), P.yunnanensis (f). Some other species tolerant (e)
Retinospora ericoides, R. pisifera filifera, not injured (f)
Retinospora (Chamaecyparis) pisifera var. filifera aurea, and var. plumosa aurea (f)
Saintpaulia ionanthus (c,d)
Sedum adophii (stonecrop). Other species tolerant (a)
Sinningia speciosa (gloxinia) (c,d)
Stephanotis floribunda (c,d)

B. FOLIATED DORMANT PLANTS

Injury has been sustained after treatments at rates shown in Schedule E.

1. PLANTS SHOWING TEMPORARY INJURY

Acer palmatum atropurpureum (Japanese maple) (c)
Daphne spp. (a)
Enkianthus campanulatus (a)
Hemerocallis spp. (day lily) (a)
Hydrangea spp. (a)
Hydrangea macrophylla (c , d)
Hydrangea paniculata (a)
Ligustrum ovalifolium (e)
Ligustrum quihoui (privet)
Ligustrum quihoui pendulum (b)
Philadelphus laxus (mock orange) (e)
Symphoricarpos chenaultii (a). Other species not injured
Tsuga canadensis pendula and T. canadensis sargentii (hemlock)(a)

2. PLANTS KILLED OUTRIGHT OR SEVERELY INJURED

Azalea var. Coral Bells, and var. Salmon Beauty (Salmon Queen) (c,d); these two varieties are quite exceptional. Azaleas generally are very tolerant (g)

Juniperus chinensis foemina (sylvestris)

Juniperus chinensis japonica

Juniperus chinensis sargentii. Partially or completely defoliated, but not killed (b)

Juniperis communis depresa plumosa

Juniperus japonica oblonga is subject to serious injury (b)

REFERENCES

(a) Donohoe and Johnson (1939)
(b) English and Turnipseed (1946)
(c) Greig (1950–56)
(d) Harper (1942–57)
(e) Latta and Cowgill (1941)
(f) Livingstone and Swank (1941)
(9) Lounsky (1939)
(h) Mackie and Carter (1937)
(i) Richardson et al (1943b)
(j) Roark (1939)

For general information see also USDA (1976) Plant Protection and Quarantine Treatment Manual, Revised April 1976, with periodic updated additions.

SCHEDULE D. METHYL BROMIDE FUMIGATION OF ACTIVELY GROWING PLANTS

The schedule is recommended for use only within the specific limits outlined below. However, in conjunction with the information on plant tolerance contained in Schedule C, it could be made the basis for experimentation on other groups of insects and varieties of plants.

MATERIAL

Glasshouse or herbaceous plants infested with armoured scales, mealy bugs, thrips, red spiders, whiteflies, aphids or leaf miners. This schedule may not be effective against soft scales and borers. For these, the vacuum fumigation treatments given in Schedule F may be attempted at the risk of plant injury.

For cyclamen mites use Schedule F. For orchids use Schedule G.

PLANT TOLERANCE

See Schedule C for list of plants sustaining injury.

Extensive experimentation on plant tolerance during the last 30 years has shown that many genera and species may be treated without injury. As a general rule, therefore, it may be said that any common glasshouse or herbaceous plant not listed among the exceptions in Schedule C may be subjected to these treatments.

Rooted cuttings of chrysanthemum are not tolerant and another method of control should be employed.

Vacuum fumigation is not recommended for actively growing plants (see remarks above concerning Schedule F).

DOSAGE

The following dosage schedule is based on Latta et al (1950). Treatments at temperatures above 30°C should be made only if unavoidable.

In conducting these treatments, the concentrations should not fall by more than 25 percent of the applied dosage in the first half hour and not by more than 50 percent during the two-hour period, e.g. for a treatment at 16 - 20°C with a dosage of 40 g/m^3 the concentration, as determined by gas analysis, at 30 minutes should be 30 g/m^3 and at 2 hours 20 g/m^3 (USDA, 1976).

ATMOSPHERIC FUMIGATION WITH METHYL BROMIDE WITH 2-HOUR EXPOSURE

TEMPERATURE		DOSAGE G/M^3 (OZ/1 000 FT^3)
°C	°F	
4 - 10	39 - 50	56
11 - 15	51 - 59	48
16 - 20	60 - 68	40
21 - 25	69 - 77	32
26 - 29	78 - 85	24
30 - 32	86 - 90	16

SCHEDULE E. METHYL BROMIDE FUMIGATION OF FOLIATED DORMANT PLANTS

A list of foliated dormant plants susceptible to injury is given in Schedule C.

MATERIAL

Broadleaved evergreens. azaleas, rhododendrons, camellias, flex, etc. Coniferous evergreens: these are susceptible to injury and care must be taken to fumigate them when fully dormant. They are particularly sensitive at the time of breaking dormancy. Exception. Araucaria - use Schedule D.

INSECTS

Two schedules are given below; the first is for external infestation generally; the second for internal feeders and species or stages of insects which are difficult to kill, such as Brachvrhinus sp. Internal feeders include such species as the European pine shoot moth Rhyscionia

ATMOSPHERIC FUMIGATION WITH METHYL BROMIDE

TEMPERATURE		DOSAGE G/M³ (OZ/L 000 FT³)	EXPOSURE PERIOD (H)	SUGGESTED MINIMUM C X T PRODUCT IN FREE SPACE OF CHAMBER (MG H/L)
°C	°F			
External infestation[1]				
4 – 10	39 – 50	40	3.5	80
11 – 15	51 – 59	40	3	72
16 – 20	60 – 68	40	2.5	64
21 – 25	69 – 77	40	2	56
26 – 29	78 – 85	32	2	48
30 – 32	86 – 90	24	2	40
Internal infestation[2] (and insects difficult to kill, such as Brachvrhinus sp.)				
4 – 10	39 – 50	64	3.5	126
11 – 15	51 – 59	64	3	114
16 – 20	60 – 68	64	2.5	102
21 – 25	69 – 77	64	2	90
26 – 29	78 – 85	48	2.5	84
30 – 32	86 – 90	40	2.5	80

[1]Dosage schedule based on Latta et al (1950) and unpublished data of Monro.
[2]Based on data of Carolin et al (1962) and unpublished data of Monro.

SCHEDULE F. METHYL BROMIDE FUMIGATION OF NONFOLIATED DORMANT PLANT MATERIAL

MATERIAL

Roots, crowns and perennials. Deciduous woody shrubs, bare-rooted fruit and shade trees. Latex-bearing plants.

INSECTS

Many species and stages of insects, including hibernating forms such as larvae of the oriental fruit moth Grapholitha molesta (Busck) in hibernaculae.

Cyclamen mites and possibly other species of leaf-feeding mites.

Brachyrhinus larvae are difficult to kill and 30 minutes should be added to the exposure period for atmospheric treatment below.

If available, vacuum fumigation may be more effective against internal insects. The schedule given for vacuum fumigation may also be generally applied for fully dormant non-foliated material.

FUMIGATION WITH METHYL BROMIDE[1]

TEMPERATURE		DOSAGE G/M³ (OZ/L 000 FT³)	EXPOSURE PERIOD (H)	SUGGESTED MINIMUM C X T PRODUCT IN FREE SPACE OF CHAMBER[2] (MG H/L)
°C	°F			
Atmospheric (for insects on the surface)				
4 – 10	39 – 50	56	4	128
11 – 15	51 – 59	48	4	116
16 – 20	60 – 68	40	4	104
21	69 and above	32	4	92
Vacuum[3] (for internal feeding insects)				
4 – 10	39 – 50	48	3.5	
11 – 15	51 – 59	48	3	
16 – 20	60 – 68	48	2.5	
21	69 and	48	2	
	above			

[1] Derived from various sources
[2] Based on unpublished data of Monro
[3] Dosage schedule based on Latta et al (1950).Vacuum is sustained at 100 mm Hg (4 in) during entire period of treatment.

SCHEDULE G. METHYL BROMIDE FUMIGATION OF ORCHIDS

MATERIAL

All orchids, collected, domestic or hybrids. Exceptions: Soft scales on non-dormant orchids and galls caused by Cecidomyid larvae should be removed by hand.

DOSAGE

TEMPERATURE		DOSAGE G/M³ (OZ/L 000 FT³)	EXPOSURE PERIOD (H)
°C	°F		
Atmospheric Schedule 1 for non-dormant orchids from greenhouse establishments, infested with armoured scales, mealy bugs, aphids, whiteflies, etc.			
4 - 10	39 - 50	56	2
11 - 15	51 - 59	48	2
16 - 20	60 - 68	40	2
21 - 25	69 - 77	32	2
26 - 32	78 - 90	24	2
Above 32	90	16	2
Atmospheric Schedule 2 for collected orchids			
4 - 10	39 - 50	48	3.5
11 - 15	51 - 59	48	3
16 - 20	60 - 68	48	2.5
21 - 25	69 - 77	48	2
26 - 32	78 - 90	40	2
Above 32	90	32	2
Partial vacuum fumigation for collected orchids of the Cattleya group, infested with Mordellistena sp., Cattleya fly, soft scales or weevil larvae; for Dendrobrium spp., infested with borers; for shipping crates with bamboo slats, infested with the bamboo shot hole borer Dinoderus minutes.			
4 - 10	39 - 50	48	3.5
11 - 15	51 - 59	48	3
16 - 20	60 - 68	48	2.5
21 - 25	69 - 77	48	2
26 - 32	78 - 90	48	1.5
Above 32	90	48	1

Operating pressure during all the above partial vacuum fumigations, 380 mm Hg (15 in)

REFERENCES

Griffin and Lubatti (1956)
Latta et al (1950)
Richardson (1949)

SCHEDULE H. METHYL BROMIDE FUMIGATION OF FRESH FRUIT AT ATMOSPHERIC PRESSURE

SPECIES AND STAGES

Caterpillars, maggots and eggs (if present) of internally feeding Diptera and Lepidoptera, and some scale insects and mites.

LITERATURE REFERENCES

Lettered references are given at the end of this schedule. For general information see also USDA (1976) with periodic revisions.

ATMOSPHERIC FUMIGATION OF FRESH FRUIT

The information given below is based on experiments or commercial experience. The tolerance data are mainly from results obtained in the temperature range 16 to 27°C at about the same dosage and exposure given in this schedule.

Tests should be made under local conditions before any schedule is drawn up and adopted.

The following schedules are for an exposure period of 2 hours.

TEMPERATURES 16 – 36°C

TEMPERATURE		DOSAGE G/M³ (OZ/L 000 FT³)
°C	°F	
16 – 20	60 – 68	40
21 – 27	69 – 81	32
28 – 32	82 – 90	24
33 – 36	91 – 96	16

Lower temperatures

So far, peaches have been found to be generally tolerant at lower temperatures, also a few varieties of apples, apricots, cherries, grapes, nectarines, pears and plums (j and o)

TEMPERATURE		DOSAGE G/M³ (OZ/L 000 FT³)
°C	°F	
4 – 10	39 – 50	64
11 – 15	51 – 59	48

FRUIT TOLERANCE TO METHYL BROMIDE

References, given after each variety, are cited at the end of this schedule.

IMPORTANT. The information on tolerance is based on fruit reaction only, and is given for guidance. It is not implied that the fumigant is necessarily effective under the given conditions against all pests found in or on the fruit. As suggested before, tests should always be made to deal with specific problems under local conditions.

Apples

Apples show considerable differences in tolerance according to varieties. Injury may be external or internal. They are usually more tolerant when picked at the proper maturity for harvesting (Phillips et al, 1938). They are less likely to be injured during the first week of cold storage, or after 6 to 8 weeks in cold storage, than during the middle of the storage period (Johnson et al, 1947).

Apple varieties not injured

Canada

BALDWIN (N.S. AND ONT.)	(i)	RHODE ISLAND GREENING (ONT.)	(i)
BEN DAVIS (N.S.)	(l)	RIBSTON (N.S.)	(i)
COX'S ORANGE (N.S.)	(i)	SPY (ONT.)	(i)
DELICIOUS* (B.C.)	(i)	STARK (N.S.)	(l)
GOLDEN RUSSET (N.S.)	(i)	WAGNER (N.S.)	(i)
KING (N.S.)	(i)	WINESAP (B.C.)	(i)
NEWTON (B.C.)	(i)		

South Africa

OHENIMURI	(c)	ROKEWOOD	(c)
PEARMAIN	(c)	YORK IMPERIAL	(c)

United States

BELLFLOWER	(b)	PARAGON	(e)
BLACK BEN DAVIS	(d)	R.I. GREENING	(d)
BLACK TWIG	(d)	RAMBO	(d)
BLAXTAYMAN	(e)	RED DELICIOUS*	(b,d,p)
COMMERCE	(d)	RED WINESAP	(b,d)
CORTLAND	(e,p)	ROME BEAUTY	(b,d,e,p)
GALLIA BEAUTY	(e)	STARK	(e)
GANO	(e)	STARKING	(d,e)
GIANT GENETON	(d)	STARR	(e)
GOLDEN DELICIOUS	(b,d,p)	STAYMEN WINESAP	(d,e)
GRAVENSTEIN	(b)	WHITE ASTRACHAN	(b)
GRIMES GOLDEN	(d)	WILLOW TWIG	(d)
JONATHAN*	(b,d,e)	WINESAP	(e)
KING DAVID	(d)	YELLOW NEWTON	(b)
LADY	(q)	YORK*	(d)
LILY OF KENT	(e)		
NORTHERN SPY	(d)		

Apple varieties injured

Canada

COX'S ORANGE (N.S.)	(i)	KING (N.S.)	(i)
FAMEUSE (QUE.)	(i)	MCINTOSH (B.C.)	(l)
JONATHAN* (B.C.)	(l)	NORTH WEST GREENING (QUE.)	(i)

India

KULU	(q)	KASHMIRI	(p)
KANDAHARI	(q)		

South Africa

RED DELICIOUS*	(c)
GRANNY SMITH	(c)

United States

DELICIOUS*	(b,e)	WEALTHY	(e)
GRIMES	(e)	(REPORTED BY THE SAME AUTHOR AS NOT INJURED IN CARLOAD FUMIGATION, 1944)	
MCINTOSH	(e)	WILLIAMS	(e)
ORLEANS	(e)	YORK*	(e)

Apricots

DERBY. SOMETIMES INJURED	(b)	TILTON. UNINJURED	(b)
ROYAL. SOMETIMES INJURED	(b,j)	UNDETERMINED VARIETIES. UNINJURED	(o)

Avocados

Dickinson, Fuerte – reported as injured (g), or uninjured (k)

Bananas

Injured, the skin turns red (m)

Cherries

The important variety Bing shows no injury from fumigation (b,j) A few other varieties may be slightly injured (b)

* Reported as tolerant by some workers and as injured by others.

Grapes Tolerant varieties

BLACK OLIVET	(f)	RIBIER	(b,f)
EMPEROR	(b)	THOMPSON SEEDLESS	(b,f)
RED MALAGA	(b)	WHITE MALAGA	(b)
PIZZUTELLO	(f)		

Not tolerant

TOKAY	(b)

Nectarines

Several varieties tolerant to schedule given here.

Peaches

Generally tolerant (b,f,h,j,k,o,p)

Pears

Generally tolerant (b,h,j,k). After fumigation fully ripe pears may break down more quickly than normal.

Plums

Reported as tolerant (h,o) or somewhat injured (b). Spotting noticed on Beauty plums when fumigated at 4°C (j).

Citrus fruit

Grapefruit and lemons are generally fairly tolerant to methyl bromide fumigation, but some injury might be expected with the schedule given here. Oranges are considerably more susceptible, showing much discoloration and spotting. At present, therefore, methyl bromide is not recommended for the fumigation of citrus fruit (see schedules J and K).

Grapefruit. Slight injury (a,g); severe injury (m,n,r,s)

Lemons. Tolerant (a)

Oranges. Valencia and Navel both spotted, discoloured, not tolerant (a,g,k,m,n,s)

REFERENCE TO FRUIT FUMIGATION

(A)	Armitage and Steinweden (1946)	(K)	Negherbon (1959)
(B)	Claypool and Vines (1956)	(L)	Phillips and Monro (1939)
(C)	Isaac (1944)	(M)	Richardson (1958)
(D)	Johnson et al (1947)	(N)	Richardson and Balock (1959)
(E)	Kenworthy and Gaddis (1946)	(O)	Richardson and Roth (1958)
(F)	Latta (1941)	(P)	Richardson and Roth (1966)
(9)	Lindgren and Sinclair (1951)	(Q)	Sen Gupta (1951)
(H)	Mackie and Carter (1940)	(R)	Hatton and Cubbedge (1979)
(I)	Monro (1941)	(S)	Benschoter (1979)
(J)	Monro (1957)		

RESIDUES

For .details of residues in fruit as the result of methyl bromide fumigation, see Getzendaner and Richardson (1966) and the review of Lindgren et al (1968).

SCHEDULE I. METHYL BROMIDE FUMIGATION OF FRESH VEGETABLES

Many kinds of fresh vegetables have been found to be tolerant to treatments with methyl bromide at intensities equal to those included in this schedule.

INSECTS

Many insects likely to be found in fresh vegetables, such as larvae of the European corn borer, adults of the Japanese beetle and pod borers of beans and peas, are susceptible to the treatments at atmospheric pressure as given below.

Larvae of fruit flies (family Trypetidae), such as the oriental fruit fly (Dacus dorsalis), require exposure of 4 h at 32 mg/l with the temperature not below 21°C (Pratt et al, 1953).

DOSAGE

ATMOSPHERIC FUMIGATION TO CONTROL INSECTS IN OR ON LEAFY VEGETABLES, EXPOSURE PERIOD 2 HOURS

TEMPERATURE		DOSAGE G/M^3 (OZ/L 000 FT^3)
°C	°F	
4 – 7	40 – 45	64
8 – 10	46 – 50	56
11 – 15	51 – 59	48
16 – 20	60 – 69	40
21 and above	70 and above	32

ATMOSPHERIC FUMIGATION OF SWEET CORN (MAIZE) ON THE COB TO CONTROL JAPANESE BEETLE AND EUROPEAN CORN BORER

TEMPERATURE		DOSAGE G/M^3 (OZ/L 000 FT^3)	EXPOSURE PERIOD, HOURS
°C	°F		
10 – 15	50 – 59	48	4
16 – 20	60 – 69	48	3
21 and above	70 and above	40	2.5

ATMOSPHERIC FUMIGATION FOR 4 HOURS OF POTATOES, SWEET POTATOES (IPOMOEA) AND YAMS (DIOSCOREA) FOR BORERS SUCH AS THE POTATO TUBER MOTH (PTHORIMAEA OPERCULELLA)

TEMPERATURE		DOSAGE G/M^3 (OZ/1 000 FT^3)
°C	°F	
21 – 26	70 – 79	56
27 – 31	80 – 89	48
32 – 36	90 – 96	40

Mackie and Carter, 1937; Lubatti and Bunday, 1958; Pradhan et al, 1960; Roth and Richardson, 1965. *Injury to some varieties of potatoes may occur at dosages of 48 g/m^3 and above at 25°C (Bond and Svec, 1977).

The following specialized schedules may be found in USDA (1976).

A. Methyl bromide in partial vacuum (380 mm or 15 in)

1. Green pod vegetables for Maruca testulalis, Epinotia aporema and Laspeyresia leguminis.

2. Root crops, including ginger.

3. Garlic for Brachycerus sp. and Dyspess ulula.

4. Cipollini bulbs for Exosoma lusitanica.

5. Horseradish for Baris lepidi.

B. Methyl bromide at atmospheric pressure. Asparagus for Halotydeus destructor, the rag-legged earth mite.

TOLERANT CROPS

IMPORTANT. The information on tolerance is based on vegetable reaction only and is given for guidance. It is not implied that the fumigant is necessarily effective under the given conditions against all the pests found in or on the vegetable. As suggested before, tests should always be made to deal with specific problems under local conditions.

Beans, lima beans (b,c); but the pods of green lima beans may be seriously injured (9); string beans (b)

Beets (c)

Cabbage (c, d)

Carrots (c)

Celeriac (knob celery) (i)

Celery (c)

Cippollini bulbs (i)

Garlic (c, h)

Horseradish (in vacuum fumigation) (i)

Maize, table (d)

Melons, Casaba

Melons, Crenshaw

Melons, watermelon (g)

Onions (c, d)

Papayas (j)

Parsnips (i)

Peas (b, c, d)

Peppers, bell (c, g)

Potatoes (c, f)

Radishes (c)

Squash, winter (g)

Sweet potatoes. Tolerant if cured 15 days or more or kiln dried for 10 days at 26 to 29°C. Newly harvested, non-cured tubers are likely to be severely injured (e).

Tomatoes (c, d, g). Delayed ripening of tomatoes may be induced by fumigation (a, g); late autumn-harvested tomatoes are less tolerant than those harvested earlier (g).

Turnips, white (c)

Yams (g), more susceptible to injury when fumigated below 21°C (i)

PARTIALLY TOLERANT CROPS (varied reaction)

Cauliflower (g)
Cucumbers (g)
Melons, Persian (g)

NONTOLERANT CROPS

The following crops are intolerant when exposed to 32 g/m^3 for 4 h at 21 to 27°C, as shown in the experiments of Pratt et al (1953)(g).

Artichokes
Beans, snap
Broccoli
Eggplants

Melons, cantaloupe
Melons, honeydew
Peppers, chilli
Squash, summer

RESIDUES

See Getzendaner and Richardson (1966) and Lindgren et al (1968).

REFERENCES

(a) Knott and Claypool (1940)
(b) Latta (1941)
(c) Mackie and Carter (1937)
(d) McLaine and Monro (1937)
(e) Phillips and Easter (1943)
(f) Pradhan et al (1960)
(g) Pratt et al (1953)
(h) Roth and Richardson (1963)
(i) Roth and Richardson (1965)
(j) USDA (1958)

General reference – USDA (1976) with periodic revision.

SCHEDULE J. ETHYLENE DIBROMIDE (EDB) FUMIGATION OF FRESH FRUIT

Ethylene dibromide (EDB) is effective against the stages of certain fruit flies (Diptera, family Trypetidae). Species found susceptible to the treatments given below are:

Anastrepha ludens (Loew). Mexican fruit fly
A. mombinpraeoptans Sein. West Indian fruit fly
A. suspense (Loew).
Ceratatitis capitata (Wied). Mediterranean fruit fly
Dacus dorsalis Hendel. Oriental fruit fly
Rhaqoletis cinqulats (Loew). Cherry fruit fly
R. pomonella (Walsh). Apple maggot

Alternative treatments – low temperature and vapour heat treatments are also used for control of these insects in fruit (see USDA, 1976).

TREATMENT FOR HAWAIIAN FRUIT

DOSAGE	EDB at 8 g/m³ (8 (oz/l 000 ft³) for 2 h with a minimum temperature of 21°C in any part of the system.
LOAD	Loading of the chamber should be limited to three quarters of the height of the chamber.
PACKAGING	Fruit may be individually wrapped in tissue paper, or packed in shredded paper or wood excelsior, in unlined corrugated cartons and sealed along the central flap with paper tape.
AUTHORITY	United States Agricultural Research Service, Plant Quarantine Branch, Administrative Instruction P.Q.592 and Amendment 1 (September, 1954 and June, 1958) (see also USDA, 1976).

TREATMENT FOR MANGOES

Dosage

TEMPERATURE		DOSAGE G/M³ (OZ/L 000 FT³)	EXPOSURE PERIOD, HOURS
°C	°F		
13 – 20	55 – 69	20	2
21 – 26	70 – 79	16	2
27 – 32	80 – 90	12	2

LOAD	The chamber should not be loaded to more than 50 percent of capacity.
PACKAGING	Mangoes may be packed in crates with shredded packing material. Wrappings must be removed before fumigation from individually wrapped fruit.
AUTHORITY	United States Department of Agriculture, Agricultural Research Service, Plant. Quarantine Branch, Administration Instruction P.Q. 608 (revised) with Amendment 1 (May 1956 and October 1956) (see also USDA, 1976).

TREATMENT OF FRUIT TO CONTROL MEXICAN FRUIT FLY

Found effective on oranges, grapefruit, tangerines, plums and mangoes.

Dosage – Ethylene dibromide in g/m³ (oz/l 000 ft³) for 2 h.

	TEMPERATURE		
FRUIT LOAD	10 – 15°C	16 – 20°C	21°C AND ABOVE
IN CHAMBER	50 – 59°F	60 – 69°F	70°F AND ABOVE
25% or less	12	10	8
26 to 49%	14	12	10
50 to 80%	16	14	12

LOAD	Load may have an important bearing on fruit tolerance to EDB. False floors vary in height and are ignored in calculating percentage load. Fruit load for plums should not exceed 50 percent the volume of the chamber.
PACKAGING	Citrus fruit may be fumigated either in bulk (field boxes) or after it has been packed in wooden boxes, paper cartons, mesh bags or plastic bags, with at least twenty 0.25 in (6 mm) holes in a 5 lb (2.27 kg) bag or a proportionate number of holes in larger bags. Fruit wrapped in tissue paper may also be fumigated.

MEDITERRANEAN FRUIT FLY IN FLORIDA

Treatments based on the foregoing schedule were used in the campaign against the Mediterranean fruit fly in Florida, beginning in May 1956 (Richardson, 1958).

Authority – U.S. Department of Agriculture, Agricultural Research Service, Plant Quarantine Division, Supplement to Quarantine 56. No.319.56 – 2 e, February 1959.

APPLE MAGGOT IN CANADIAN APPLES

Fumigation of apples with EDB at fruit and air temperatures above 16°C in approved chambers or under gas proof sheets to control larvae of the apple maggot Rhanoletis pomonella.

Dosage – EDB 6 mg/l (6 (oz/l 000 ft³) for 2 h (Sanford, 1962a, b). (At temperatures below 10°C there may be considerable persistence of EDB vapours.)

GENERAL NOTES CONCERNING TREATMENT OF FRUIT WITH EDB

1. The ethylene dibromide must be volatilized as quickly as possible by means of pans on hot plates or by other effective vaporizing devices.

2. The fumigation period required begins when all the fumigant is known to have evaporated. (This time may be determined by experiment or by observation through glass ports.)

3. Circulation of the fumigant/air mixture by means of fans or blowers must continue throughout the exposure period.

4. Thorough aeration of the fruit is essential before it is released for human consumption. This is especially important in the fruit temperature range of 10 to 27°C.

TOLERANCE OF FRUIT TO EDB FUMIGATION

The tolerance of the fruit listed below was determined by exposure to 16 g/m^3 (16 (oz/l 000 ft^3) for 2 h at 21°C unless otherwise stated. Therefore, these fruits should be tolerant under normal circumstances to any of the schedules given above.

IMPORTANT. The information on tolerance is based on fruit reaction only and is given for guidance. It is not implied that the fumigant is necessarily effective under the given conditions against all pests found in or on the fruit. As suggested before, tests should always be made to deal with specific problems under local conditions.

TOLERANT FRUITS

Apples, numerous United States varieties (a, 9, j). Apples, 5 Canadian varieties (k). (Apples appear to be generally tolerant to EDB.)

Apricots (3 varieties)(a)

Avocados (a). No injury at 0.5 to 3 lb/1 000 ft^3 (c); no injury to Fuerte avocados at 1 to 3 lb (f); MacArthur, Anaheim and El Tropico were injured at 2 lb/1 000 ft^3 for 2 h; 3 lb caused severe injury(f).

Bananas, Cavendish (i)

Cherries (3 varieties) (a, d)

Citrus: grapefruit, lemons, oranges and tangerines are tolerant if recommendations are followed (c,e). Overloading the chamber may result in peel injury, especially in grapefruit.

Figs (2 varieties) (a)

Grapes (6 varieties) (a)

Mangoes (c, h). Tolerant at 1 lb/1 000 ft³ for 2 h at 25°C (c, l) Nectarines (6 varieties) (a)

Papayas (e)

Peaches (13 varieties) (a, j) Pears (6 varieties) (a, j)

Pineapples (e)

Plums (16 varieties) (a, j)

NON TOLERANT FRUITS

Avocados (some varieties)
Persimmons (5 varieties) (a)

RESIDUES

For details of residues see Tanada et al (1953), Dumas (1962), Coggiola and Huelin (1964), Alumot et al (1965) and the general reviews of Lindgren et al (1968) and Dumas and Bond (1975).

REFERENCES

(A)	Claypool and Vines (1956)	(G)	Richardson (1952)
(B)	Grierson and Hayward (1959)	(H)	Richardson (1955)
(C)	Grundberg et al (1956)	(I)	Richardson and Balock (1959)
(D)	Jones (1955)	(J)	Richardson and Roth (1966)
(E)	Lindgren and Sinclair (1951)	(K)	Sanford (1962a, b)
(F)	Lindgren et al (1955)	(L)	Shaw and Lopez (1954)

General references – USDA (1967b) and USDA (1976) with periodic revisions.

SCHEDULE K. ETHYLENE DIBROMIDE(EDB) FUMIGATION OF FRESH VEGETABLES

Ethylene dibromide (EDB) is effective against the stages of certain fruit flies (Diptera, family Trypetidae) which may be found in certain vegetables.

Species of insects found susceptible are listed in Schedule J together with general notes on ethylene dibromide fumigation of perishable materials.

TREATMENT

A standard treatment, effective against the oriental fruit fly, Dacus dorsalis, is EDB at a dosage 8 g/m^3 (8 (oz/1 000 ft^3) for 2 h with a minimum temperature of 21°C in any part of the system. The load factor given for Mexican fruit fly in Schedule J could be applied.

TOLERANCE OF FRESH VEGETABLES TO EDB

The reactions listed below are based on Pratt et al (1953) with the treatment given above.

IMPORTANT. The information on tolerance is based on vegetable reaction only and is given for guidance. It is not implied that the fumigant is necessarily effective under the given conditions against all pests found in or on the vegetable. As suggested before, tests should always be made to deal with specific problems under local conditions.

TOLERANT CROPS

Beans, lima and snap
Broccoli
Cucumbers
Melons (cantaloupe, casaba, honeydew, Persian, watermelon)
Peppers, bell
Squash (summer and winter varieties)

NON TOLERANT CROPS

Artichokes. Discoloration and decay Cauliflower. Darkening and spotting of curds; killing of leaves Eggplant. Severe general injury Melon, Crenshaw Peppers, chill). Injury to calyx and off-colour of fruit Tomatoes (4 varieties)

RESIDUE TOLERANCES

The general review of Lindgren et al (1968) discusses official United States tolerances for ethylene dibromide used on a number of vegetables.

SCHEDULE L. HYDROGEN CYANIDE (HCN) FUMIGATION OF FRESH FRUIT AND VEGETABLES

Some fruits are tolerant to HCN and, if applied according to directions, the fumigant may be used on them without danger to the consumer. Applications recommended for certain quarantine purposes are given here.

ATMOSPHERIC FUMIGATION WITH HCN

The fumigant volatilized from the liquid is applied at the rate of 6 g/m³ (6 (oz/l 000 ft³) for one hour at a temperature above 10°C. Fan circulation (explosion-proof motors) must be maintained throughout the treatment. The fruit must be dry, otherwise serious burning may result.

Avocados, packed for shipment, to control latania scale, Hemiberlesia lataniae (Sign.)

Citrus fruit (oranges, lemons, limes, grapefruit) to control scale insects and thrips and possibly other external pests such as citrus whitefly and black fly. For control of bean thrips, Hercothrips fasciatus (Perg.), exposure period may be reduced to 35 minutes (Harper, 1942 - 57; Richardson and Balock, 1959).

HCN is used extensively in Japan for fumigation of bananas and citrus fruit infested with scale insects (Mori, 1980). Application is conducted through a dispenser unit consisting of a vaporizer and blower and the gas is circulated to facilitate even distribution. After fumigation, the remaining gas is removed through an HCN gas scrubber. The recommended dosage is 2 g/m³ for 30 min.

VACUUM FUMIGATION WITH HCN (Harper, 1942 - 57)

Dosage 6 g/m³. The fumigant introduced into initial vacuum of 125 mm (about 5 in) absolute pressure with stream of air (simultaneous introduction) until atmospheric pressure is reached. Exposure period: 1 hour. Temperature not less than 15°C.

For control of mealy bugs, Pseudococcus sp., in persimmons packed for export

SCHEDULE M. HYDROGEN CYANIDE (HCN) FUMIGATION OF DORMANT NURSERY STOCK

Balled nursery stock should be held for 10 to 14 days after digging before fumigation. Avoid free moisture on plants. After fumigation, all plants should be gently but thoroughly washed by sprinkling with water. They should be protected from sunlight and wind for 48 h following treatment.

ATMOSPHERIC FUMIGATION WITH HCN

Fumigation of imported nursery stock to prevent introduction of San Jose scale, Aspidiotus perniciosus Comst. Dosage HCN 6 g/m³ (6 oz/l 000 ft³). Temperature not below 4 C. Fumigant is introduced with stream of air. After this, continuous recirculation of fumigant/air mixture in the chamber at a rate per hour equivalent to 40 times the cubic capacity of the chamber. Exposure period: 30 min.

The above is based on information supplied by the Netherlands Ministry of Agriculture, Plant Protection Service (Personal communication P.H. Van de Pol, 17 March 1959).

If the above rate of circulation of fumigant/air mixture cannot be attained, apply the treatment used for many years to control scale insects and woolly aphids before the introduction of Vacuum fumigation or high velocity circulation. Dosage of HCN, 10 g/m³ (10 oz/l 000 ft³). Temperature not less than 4 C. Exposure period: 45 min to 1 h. Continuous circulation of air/fumigant mixture is advisable. If fans or blowers are used, they should be of the shielded, nonexplosive type.

For discussion of technical problems in the fumigation of plant material with HCN, see Be ran (1946) and Van de Pol and Rauws (1957).

VACUUM FUMIGATION WITH HCN (Harper 1942 - 57)

Fumigation of balled citrus plants to control scale insects, specifically the Californian red scale, Aonidiella aurantii (Mask.). Dosage of HCN 5 g/m³ (5 oz/l 000 ft³). Temperature not less than 10°C. Initial vacuum 100 mm (4 in) of Hg absolute pressure. Fumigant is introduced with stream of air until atmospheric pressure is restored. Exposure period: 1 h.

SCHEDULE N. FUMIGATION OF FLOWER BULBS AND CORMS

This schedule covers flower bulbs and corms, including bulbous iris, gladioli, lilies (including Easter lilies), narcissus, tulips and many other kinds.

VACUUM TREATMENTS

Some varieties may be affected by sustained vacuum and produce short stemmed plants or retarded growth. Initial vacuum treatments followed by restoration of atmospheric pressure after or during the introduction of the fumigant are usually effective and less injurious to bulbs.

1. For aphids (tulip bulb aphid, Anuraphis tulipae (Fonsc.), and other species).

(a) HCN. 10°C and above; 2 g/m³ (2 oz/l 000 ft³) for 2 h under atmospheric pressure.

(b) Methyl bromide. See schedule for mites. Aphids are easily killed by methyl bromide but stronger treatment will also control postembryonic mites.

2. For bulb flies, narcissus bulb fly, Lampetia equestris (F.), and lesser bulb fly, Eumerus tuberculatus Rond.).

(a) HCN. 18°C and above: 6 g/m³ for 6 h under atmospheric pressure (recommended by the Netherlands Ministry of Agriculture).

(b) Methyl bromide. 15 to 20°C: 48 g/m³ for 5 h under atmospheric pressure, or 48 g/m³ for 3 h under preliminary vacuum.

21°C and above: 48 g/m³ for 4 h under atmospheric pressure or 48 g/m³ for 2.5 h under preliminary vacuum.

Below 15°C: not recommended for atmospheric fumigation (Andison and Cram, 1952).

3. For mites (bulb mite, Rhizoalyphus echinopus (F. & R.), bulb scale mite, Steneotarsonemus laticeps (Halb.), eriophyid mites). Methyl bromide treatment should be repeated after 10 to 14 days in order to kill eggs (Mackie et al, 1942; Monro, 1937 – 40). Eriophyid mites, Eriophyes spp., may sometimes be controlled by milder treatments with HCN or methyl bromide.

(a) HCN. 18°C and above: 6 g/m³ for 24 h (recommended by the Netherlands Ministry of Agriculture).

(b) Methyl bromide. 15 to 21°C: 48 g/m³ for 2.5 h under atmos pheric pressure, or 48 g/m³ for 2 h under preliminary vacuum.

21 to 27°C: 48 g/m³ for 2 h under atmospheric pressure, or 48 g/m for 1.5 h under preliminary vacuum.

27°C and above: 40 g/m³ for 2 h under atmospheric pressure, or 40 g/m³ for 1.5 h under preliminary vacuum.

4. For thrips (gladiolus thrips, Taeniothrips simplex (Mor.) and lily bulb thrips. Liothrips vaneeckei Pries.). With methyl bromide against thrips, temperature is an important factor in obtaining complete control of the insects in all stages, including eggs. It is advisable, wherever possible, to fumigate at or above 20°C (Steinweden et al (1942).

Methyl bromide. 21 to 27°C: 48 g/m³ for 3 h under atmospheric pressure, or 48 g/m³ for 2 h under preliminary vacuum.

27°C and above: 48 g/m³ for 2 h under atmospheric pressure, or 40 g/m³ for 2 h under preliminary vacuum.

General reference – USDA (1976) with periodic revisions.

SCHEDULE O. METHYL BROMIDE FUMIGATION OF CUT FLOWERS AND GREENERY

THRIPS

Methyl bromide at the rate of 16 g/m³ (16 oz/l 000 ft³) for 1.5 h may be applied to cut flowers of rose, tulip and carnation at atmospheric pressure at temperatures of 29 to 31°C for the control of thrips, Rhiphiphorothrips cruentatus H., without injuring the blooms (Junaid and Nasir, 1956).

Chrysanthemums (aphids only), methyl bromide 12 g/m^3 (12 $oz/l\ 000\ ft^3$) for 2 h at 21 C or above.

SURFACE FEEDERS, LEAF MINER, THRIPS.

Methyl bromide At atmospheric pressure exposure period 2 hours

TEMPERATURE		DOSAGE G/M^3 ($OZ/L\ 000\ FT^3$)
°C	°F	
4 – 9	40 – 49	56
10 – 15	50 – 59	48
16 – 20	60 – 68	40
21 – 26	70 – 79	32
27 – 36	80 – 96	24

Concentrations should be at least 75 percent of the applied dosage at 30 min and 50 percent at 2h.

BORERS, SOFT SCALES (VACUUM FUMIQATION – 380 MM)

TEMPERATURE		DOSAGE G/M^3 ($OZ/1\ 000\ FT^3$)	EXPOSURE TIME (H)
°C	°F		
4 – 9	40 – 49	48	3.5
10 – 15	50 – 59	48	3
16 – 20	60 – 68	48	2.5
21 – 26	70 – 79	48	2
27 – 32	80 – 90	40	2

The prior consent of the importer should be obtained for vacuum fumigation.

See USDA (1976) for further information on these treatments.

SCHEDULE P. ATMOSPHERIC AND VACUUM FUMIGATION FOR THE CONTROL OF PESTS INFESTING PACKAGED PLANT PRODUCTS

This schedule covers a wide range of plant products, including grains, in packages such as bags (sacks), cartons, boxes and bales, which are permeable to the fumigants named. Bulk fumigation of certain agricultural and forest products is also included.

The success of the treatments given here will depend on the proper conduct of the procedures described in the text end on the provision of gas tight conditions in the structures employed. Adequate retention of fumigant must be checked by gas analysis; this is especially important in fumigation under sheets.

ATMOSPHERIC FUMIGATION CHAMBERS

All the fumigants named for the specific products may be used in specially designed and properly equipped atmospheric chambers as described in the text.

SHEETED FUMIGATIONS

At present most treatments under gas-proof sheets at atmospheric pressure are carried out with methyl bromide or phosphine and careful testing is required before other fumigants are used for treating specific materials.

OTHER STRUCTURES

Treatments under atmospheric pressure may be applied in a variety of structures, which can be rendered sufficiently gas tight, such as the holds of ships and barges, trucks, trailers, railway cars (wagons) and rooms in warehouses and other buildings. Methyl bromide and phosphine are mainly employed but HCN may be applied under certain conditions as described below. Other fumigants, such as the ethylene oxide/carbon dioxide mixture, have specialized applications.

VACUUM FUMIGATION

The operating pressure recommended for sustained vacuum fumigation, after the fumigant is introduced, is from 75 to 125 mm (3 to 5 in)of mercury. (This does not apply to the ethylene oxide/carbon dioxide mixture 1:9, which increases the pressure considerably.)

The pressure manipulations described in Chapter 9, which involve various alterations in the pressure of the chamber subsequent to the attainment of the initial vacuum, may be tested for different fumigants on different materials. No specific recommendations can be made before preliminary trials are made. The treatments given here are all for exposures under sustained vacuum.

CIRCULATION

Circulation of the fumigant in the space should be effected whenever possible. This may be done by fans or, in specially designed chambers, by means of recirculation systems. Circulation is necessary in vacuum fumigation - it is usually done for 15 min at the beginning of each hour of treatment. In atmospheric fumigation, circulation for at least 30 min at the beginning of the treatment is advisable (see text). In small-scale atmospheric fumigation of begged material, such as in railway cars or under small

covers or tarpaulins, circulation may be omitted if adequate distribution of the fumigant is ensured by other means (see text).

PERMEABILITY OF PACKAGING MATERIALS

Many materials used for packaging are readily permeable to fumigants under the conditions recommended below. Phosphine diffuses readily, even at comparatively low temperatures. According to Roth and Richardson (1968) common brown (kraft) paper, glazed papers and corrugated cardboard are easily penetrated by methyl bromide; tar, laminated and wax papers, polyethylene films, masking tape and wallboard have comparatively low permeability to this fumigant.

A. Stored product pests in general

1. EMPTY BAGS MADE FROM JUTE (BURLAP) OR OTHER MATERIALS

(a) Loose, non-compressed bales or bundles

Methyl bromide. 15°C sod above: 24 to 32 g/m^3 (24 to 32 oz/l 000 ft^3) for 16 to 24 h under atmospheric pressure, or 40 g/m^3 for 3 h under sustained vacuum. For control of Khapra beetle, Troqoderma qranarium Everts, the United States Department of Agriculture requires doubled dosage for vacuum fumigation and quadrupled dosage for atmospheric pressure treatment.

(b) Compressed bales

Methyl bromide. 15°C and above: 56 g/m^3 for 4 h under sustained vacuum. Owing to high degree of sorption of vapours by material, care must be taken by operators to avoid inhalation of methyl bromide during unloading. After unloading, keep bales in well ventilated storage for at least 4 days.

2. PERMEABLE CARTONS, PACKAGES OR BAGS OF CEREALS

Containers should be tested for permeability. Heat-sealed cellophane polyethylene, wax paper or tar paper wrappings may not permit adequate penetration, even under vacuum fumigation.

(a) Methyl bromide

Under atmospheric pressure: 48g/m^3 for 16 to 24 h at 10 to 14°C; 40g/m^3 for 16 to 24 h at 15 to 20°C; 32g/m^3 for 16 to 25 h at 21 to 25°C or 24g/m^3 for 16 to 24 h at 25°C and above. Under sustained vacuum 40g/m^3 for 3 h at 15°C and above.

(b) Hydrogen cyanide (HCN)

Under sustained vacuum: 2.5 g/m^3 for 3 h at 20°C and above.

(c) Phosphine

At atmospheric pressure: sufficient of an aluminium or magnesium phosphide formulation to generate 1.5 9 of phosphine per m should be applied. Period of fumigation should be 7 days at 12 to 15°C, 6 days at 16 to 20°C, 5 days at 21 to 25°C or 4 days at 26°C or above.

(d) Ethylene dibromide (EDB)/methyl bromide mixture

At atmospheric pressure under tropical conditions: 16 to 32 g/m^3 (16 to 32 oz/l 000 ft^3) of 1:1 (w/w) mixture for 48 hours. At temperatures below 26°C 1:3 mixture of EDB to methyl bromide should be applied (Majumder and Muthu, 1964).

3. PERMEABLE CARTONS OR PACKAGES OF MILK POWDER

(a) Ethylene oxide/carbon dioxide mixture (1:9)

Suggested for vacuum fumigation at 720g/m^3 for 3 h at 20°C and above. (See text for discussion of residues).

(b) Methyl bromide

Atmospheric pressure: see 2 (a) above.

(c) Phosphine

Dosage and exposure 2 (c) above.

4. PERMEABLE CARTONS OR OTHER CONTAINERS OF LOOSE RAISINS, CURRANTS, DATES, FIGS OR OTHER DRIED FRUIT

(a) Methyl bromide

Under atmospheric pressure: 24 g/m^3 for 24 h at 15°C and above. Under sustained vacuum: 40 g/m^3 at 15°C and above for 3 h. For lepidopterous pests, exposure in vacuum fumigation may be reduced to 2 h at temperatures above 20°C3. For fumigation under sheets or kraft paper over soil base, 32 g/m^3 are recommended.

(b) Ethylene oxide/carbon dioxide mixture (1:9)

Under sustained vacuum: 640 g/m^3 for 3 h at 20°C and above. (See text for discussion of residues.)

(c) Phosphine

At atmospheric pressure 1 9 phosphine per m^3 of storage space.

5. PERMEABLE CARTONS OF DRIED FRUIT, INCLUDING DATES AND FIGS, IN COMPRESSED FORM

(a) Methyl bromide

Under sustained vacuum: 40 g/m³ for 3 h at 20°C and above.

(b) Ethylene oxide/carbon dioxide mixture (1:9)

Under sustained vacuum: 800 g/m³ for 4 h at 20°C and above. (See text for discussion of residues.)

(c) Phosphine

At atmospheric pressure see 4 (c) above.

6. PERMEABLE CONTAINERS OF FLOUR, MEALS, FEEDS, MIXED FEEDS AND MILLED CEREALS

(a) Methyl bromide

Under atmospheric pressure 48 g/m³ for 16 to 24 h at 10 to 14°C; 32 g/m³ for 16 to 24 h at 15 to 20°C;24 g/m³ for 16 to 24 h at 20 to 25°C or 16 g/m³ for 16 to 24 h at 25°C and above Under sustained vacuum: 48 g/m³ for 3 h at 20°C to 25°C; or 40 g/m³ for 3 h at 25°C and above. With flours, great care must be taken to avoid over dosage, which may be brought about through poor distribution of fumigant in a given load. To avoid this, fans or a recirculation system must be properly used.

Off-odours in bread and flour as a result of methyl bromide fumigation have occasionally been reported (see full discussion in text).

(b) Phosphine

Under atmospheric pressure: Sufficient of an aluminium or magnesium phosphide formulation to generate 1.5 9 of Phosphine per m . Fumigate for 7 days at 12 to 15°C, 6 days at 16 to 20°C, 5 days at 21 to 25°C or 4 days at 26°C or above.

(c) Ethylene dibromide (EDB)/methyl bromide mixture

At atmospheric pressure under tropical conditions 32 to 48 g/m³ of 1:3 EDB:methyl bromide mixture w/w for 48 to 72 h (Majumder and Muthu, 1964).

(d) Ethylene oxide/carbon dioxide mixture (1:9)

Under sustained vacuum: 800g/m³ for 6 h at 25°C and over. (See text for discussion of residues.)

(e) Hydrogen cyanide (HCN)

Under sustained vacuum: 40g/m³ for 3 h at 20°C and over.

(f) Chloropicrin

Under atmospheric pressure: 32 to 48g/m³ for 24 h at 20°C and over. Higher dosages may be required for densely packed materials. This recommendation is subject to trial under local circumstances. Considerable time is required for ventilation.

7. BAGGED BARLEY, MAIZE, OATS, RICE, RYE, WHEAT AND OTHER GRAINS, ALSO DRIED BEANS, PEAS AND COCOA BEANS

(a) Methyl bromide

Under atmospheric pressure 40g/m³ for 16 to 24 h at 4 to 9°C; 32g/m³ for 16 to 24 h at 10 to 14°C; 24g/m³ for 16 to 24 h at 15 to 20°C or 16g/m³ for 16 to 24 h at 21°C and above. Under sustained vacuum. 56g/m³ for 3 h at 4 to 9°C; 48g/m³ for 3 h at 10 to 14°C; 40g/m³ for 3 h at 15 to 20°C; or 32g/m³ for 3 h at 21°C and above.

(b) Phosphine

Under atmospheric pressure: Sufficient of an aluminium or Magnesium phosphide formulation to generate 1.5 9 of phosphine per m . Fumigate for 7 days at 12 to 15°C, 6 days at 16 to 20°C, 5 days at 21 to 25°C or 4 days at 26°C or above (Heseltine and Thompson, 1957; Harada, 1962; Hubert,1962; Pingale et al, 1963; Cogburn and Tilton, 1963; Rai et al, 1962; Lochner, (1964a).

(c) Ethylene dibromide (EDB)/methyl bromide mixture

Under tropical conditions at atmospheric pressure: use treatments given in 2 (d) above.

(d) Hydrogen cyanide (HCN)

Under atmospheric pressure: 32g/m³ for 24 h at 20°C and above. Under sustained vacuum: 40g/m³ for 3 h at 20°C and above. For rice, see Redlinger (1957c).

(e) Chloropicrin

Under atmospheric pressure: 48g/m³ for 24 h at 20°C and above.

(f) Ethylene dichloride/carbon tetrachloride mixture (3:1)

Under atmospheric pressure: 480g/m³ for 24 h at 20°C and above; or 360 g/m for 48 h at 20°C and above.

(g) Ethylene dibromide

Under atmospheric pressure: 75g/m³ for 24 h at 25°C and above. Suggested from work in India for use under tarpaulins at 240 9/1 000 bags (Pingale and Swaminathan, 1954). See discussion in text.

8. NUTS, SHELLED (NUTMEATS) OR IN THE SHELL: ALMONDS, BRAZIL NUTS, BUTTERNUTS, CASHEW NUTS, CHESTNUTS, FILBERTS (HAZELNUTS), HICKORY NUTS, PECANS, GROUNDNUTS, PISTACHIO NUTS AND WALNUTS.

(a) Methyl bromide

Under atmospheric pressure 48g/m³ for 16 to 24 h at 4 to 9°C; 49 g/m for 16 to 24 h at 10 to 14 C; 32g/m³ for 16 to 24 h at 15 to 20°C; 24g/m³ for 16 to 24 h at 21 to 25°C or 16 to 24g/m³ for 16 to 24 h at 25°C and above. Under sustained vacuum: 56g/m³ for 3 h at 4 to 9°C; 48g/m³ for 3 h at 10 to 14°C; 40g/m³ for 3 h at 15 to 20°C; 32g/m³ for 3 h at 21 to 25°C; or 24g/m³ for 3 h at 25°C and above. With lepidopterous pests, exposure in vacuum fumigation may be reduced to 1.5 or 2 h when the temperature is 20°C or above.

(b) Hydrogen cyanide (HCN)

Under atmospheric pressure: 32g/m³ for 24 h at 20°C and above. Under sustained vacuum: 40g/m³ for 3 h at 20°C and above.

(c) Chloropicrin

Under atmospheric pressure: 48g/m³ for 24 h at 20°C and above. Very thorough aeration required.

(d) Ethylene oxide/carbon dioxide mixture (1:9)

Under sustained vacuum: 560 to 640g/m³ for 3 h at 20°C and above. Use the higher dosage for nuts in shells and for nuts packed in cartons. (See text for discussion of residues.)

(e) Ethylene dichloride/carbon tetrachloride mixture (3:1)

Under atmospheric pressure: 400g/m³ for 48 h at 20°C and above; or 640 g/m for 24 h at 20°C and above. Recommended for well constructed fumigation chambers only.

(f) Phosphine

Under atmospheric pressure: Sufficient of an aluminium or magnesium phosphide formulation to generate 1.5 9 of phosphine per m3.

9. SPICES OF ALL KINDS

(a) Methyl bromide

Under atmospheric pressure: 16 to 24g/m³ for 16 to 24 h at 20°C and above. Under sustained vacuum: 40g/m³ for 3 h at 20°C and above. Treatment at lower temperatures may be practicable, following the schedule for cereals.

(b) Hydrogen cyanide (HCN)

Under atmospheric pressure: 24 to 32g/m³ for 24 h at 20°C and above. Under sustained vacuum 40 g/m for 3 h at 20°C and above.

(c) Phosphine

Under atmospheric pressure: Sufficient of an aluminium or Magnesium phosphide formulation to generate 1.5 9 of phosphine per m . Fumigate for 7 days at 12 to 15°C, 6 days at 16 to 20°C, 5 days at 21 to 25°C or 4 days at 26°C or above.

(d) Ethylene dibromide (EDB)/methyl bromide mixture

Under tropical conditions at atmospheric pressure; use schedule given in 2 (d) above.

(e) Ethylene oxide/carbon dioxide mixture (1:9)

Under sustained vacuum: 640g/m³ for 3 h at 20°C and above.

B. Golden nematode (Heterodera rostochiensis), in loose or compressed bales or bags made from jute (burlap) or other materials

Methyl bromide

Under atmospheric pressure: 368g/m³ for 16 h at 10°C and above. Atmospheric fumigation only effective for loose bales or bundles (Lear and Mai, 1952).

United States Department of Agriculture (USDA, 1976) only lists sustained vacuum treatments as follows:

Methyl bromide in 26 in vac (100 mm abs. press.); 128g/m³ for 16 h at 4 C and above; 168g/m³ for 12 h at 4°C and above; 256g/m³ for 8 h at 4°C and above; add 32 9 and 2 h at -1 to 4°C, add 48 9 and 4 h at -7 to 2OC; add 48 9 and 6 h at -12 to -8OC.

C. European Corn Borer (0strinia nubilalis), species of Sesamia and other lepidopterous borers in non-perishable products

Also a wide variety of agricultural pests which may enter the following materials incidentally or for hibernation (Monro, 1947b): broom corn and maize stalks in bales

or bundles (stalks and panicles of Sorqhum vuluare var. technicum or stalks of Zea mays or related plants).

(a) Methyl bromide

Under atmospheric pressure: 112g/m³ for 16 h at 5 to 9°C; 80g/m³ for 16 h at 10 to 14°C or 40g/m³ for 16 h at 15°C and above. Under sustained vacuum: 96g/m³ for 2.5 h at 0 to 4°C; 80g/m³ for 2.5 h at 5 to 9°C; 64g/m³ for 2.5 h at 10 to 14°C; or 40g/m³ for 2.5 h at 15°C and above.

(b) Hydrogen cyanide (HCN)

Under sustained vacuum 48g/m³ for 3 h at 15°C and above.

D. Pink Bollworm, Pectinophora qossypiella, and other insects infesting cotton

1. COTTON IN BALES, LOOSE OR HYDRAULICALLY PRESSED

Hydrogen cyanide (HCN)

Under sustained vacuum: 40g/m³ for 2 h at 15°C and above. U.S. Department of Agriculture Regulation HB-164 (March 1923) stipulates that after the introduction of the fumigant into the evacuated chamber, the pressure in the chamber be raised to 125 mm (5 in) of mercury by the introduction of air; and that the pressure be kept at this level until the end of the 2-hour exposure.

2. COTTONSEED BAGGED OR PACKAGED

Methyl bromide

Under atmospheric pressure: 64g/m³ for 24 h at 4 - 15°C or 48g/m³ for 24 h above 15°C. Under sustained vacuum: 64g/m³ for 2 h at 4°C and above (load limit 50 percent of chamber volume).

Hydrogen cyanide (HCN)

Under vacuum, 100 mm absolute pressure: 60g/m³ for 2 h at 4°C or above (load limit 50 percent of chamber volume).

Phosphine

Sufficient of an aluminium or magnesium phosphide formulation to generate 2 9 of phosphine per m ; for 5 to 7 days at 10°C or above.

3. EXTERNAL FUMIGATION OF COTTON BALES

The Government of India requires that all bales of American cotton entering that country should be subjected to atmospheric fumigation with hydrogen cyanide to control the boll weevil (Anthonomus qrandis Bob.) or other insects which may be found on or near to the surface of the bales (Liston, 1920; Liston and Gore, 1923; Turner and Sen, 1928).

E. Hay, baled, including Lucerne (Alfalfa) hay

ALFALFA WEEVIL, Hypera postica (Gyll.)

Methyl bromide

Under atmospheric pressure: 32g/m³ for 16 to 24 h at 15°C and above. Under sustained vacuum: 40g/m³ for 3 h at 15°C and above. Vacuum fumigation probably not economically feasible.

2. CEREAL LEAF BEETLE, OULEMA MELANOPUS (KIRBY)

United States and Canada: Department of Agriculture schedules. Methyl bromide

TEMPERATURE		DOSAGEG/M³ (OZ/L 000 FT³)	EXPOSURE PERIOD HOURS
°C	°F		
–18 to –7	0 – 19	104	4
– 6 to –2	20 – 29	96	4
– 1 to +9	30 – 49	64	4
10 to 20	50 – 69	40	3
21 and above	70 and above	32	3

F. Cigarette Beetle, Lasioderma serricorne, (F.) and Tobacco Moth, Ephestia elutella (Hbn)

1. ALL TYPES OF CIGARETTE TOBACCO

With these types in hogsheads and bales, atmospheric pressure cannot be relied upon for complete mortality, even with very long exposure periods, except with the fumigant phosphine. Vacuum fumigation using other fumigants is effective with bales, hogsheads and most packages (Tenhet, 1957).

(a) Hydrogen cyanide (HCN)

Under atmospheric pressure: 24g/m³ for 48 to 72 h at 7 to 20°C; or 16g/m³ for 48 to 72 h at 21°C and above. Under sustained vacuum: 84g/m³ for 4 h at 7 to 20°C; or 64g/m³ for 4 h at 21°C and above.

(b) Methyl bromide

Under atmospheric pressure: 32g/m³ for 48 to 72 h at 7 to 20°C; or 20g/m³ for 48 to 72 h at 21°C and above. Under sustained vacuum: 80g/m³ for 4 h at 7 to 20°C; or 64g/m³ for 4 h at 21°C and above.

(c) Acrylonitrile/carbon tetrachloride (1:2)

Under atmospheric pressure: 56 to 80g/m³ for 48 to 72 h at 7 to 20°C or 48 to 64g/m³ for 48 to 72 h at 21°C and above. under sustained vacuum: 80g/m³ for 4 h at 7 to 20°C; or 64g/m³ for 4 h at 21°C and above.

(d) Phosphine

Sufficient of an aluminium or magnesium phosphide formulation to generate 0.67 to 1 9 of phosphine per m .

2. CIGARS AND CIGAR TOBACCOS, EXCEPT CIGARS WRAPPED IN BALES

Vacuum fumigation effective for boxes of cellophane cigars and sealed cartons of boxes of cigars. Impractical to fumigate satisfactorily boxes of cigars over wrapped in cellophane (Tenhet, 1957). Methyl bromide not recommended for cigar tobaccos because off-odour sometimes results.

(a) Hydrogen cyanide (HCN)

Under atmospheric pressure: 24g/m³ for 48 to 72 h at 7 to 20°C; or 16g/m³ for 48 to 72 h at 21°C and above Under sustained vacuum: 80g/m³ for 4 h at 7 to 20°C; or 64g/m³ for 4 h at 21°C and above.

(b) Acrvionitrile/carbon tetrachloride (1:2)

Under atmospheric pressure: 56 to 80g/m³ for 48 to 72 h at 7 to 20°C or 64 to 80g/m³ for 48 to 72 h at 21°C and above. Under sustained vacuum: 80g/m³ for 4 h at 7 to 20°C; or 64g/m³ for 4 h at 21°C and above.

(c) Ethylene oxide/carbon dioxide (1:9)

Under sustained vacuum: 960g/m³ for 4 h at 21°C and above.

3. CIGARS WRAPPED IN BALES

(a) Hydrogen cyanide (HCN)

Under atmospheric pressure: 24g/m³ for 48 to 72 h at 21°C and above. Under sustained vacuum: 80g/m³ for 4 h at 21°C and above.

(b) Acrvionitrile/carbon tetrachloride (1:2)

Under atmospheric pressure: 64 to 80g/m³ for 48 to 72 h at 21°C and above. Under sustained vacuum: 80g/m³ for 4 h at 21°C and above.

(c) Ethylene oxide/carbon dioxide (1:9)

Under sustained vacuum: 1 040g/m³ for 4 h at 21°C and above.

G. Wood-boring beetles and wood wasps in timber cut in board lengths

Methyl bromide

Under atmospheric pressure: 32g/m³ for 24 to 36 h at 15°C and above. Fumigation may be carried out under gas-proof sheets and in the holds of ships (Burden and McMullen, 1951). Good distribution of fumigant is essential. Vacuum fumigation probably not economically feasible.

H. Mangolds

Methyl bromide

Fumigation of mangolds in clamps (piles) to control aphid vectors of virus yellows (Dunning et al 1962). Methyl bromide under gas-proof sheet for a minimum of 3 h to effect a c x t product 100 mg in/l.

I. General references to plant product treatments

Treatments

USDA (1976, 1977 and updated revisions).

Residues

Lindgren et al (1968).

SCHEDULE Q. FUMIGATION OF MILLS, EMPTY STRUCTURES AND TOBACCO WAREHOUSES

Mills and empty structures that may be made sufficiently gas tight for atmospheric fumigation, including warehouses, empty holds of ships and other carriers (for treatment of most structures containing goods, see Schedule P).

1. SEALED BUILDINGS (MILLS, EMPTY WAREHOUSES AND SIMILAR BUILDINGS)

For eradication of residual populations of stored product insects and similar pests.

(a) Methyl bromide

40 to 48g/m^3 for 24 h at O to 4°C; 32 to 40g/m^3 for 24 h at 5 to 9°C; 24 to 32g/m^3 for 24 h at 10 to 14°C; or 16 to 24g/m^3 for 24 h at 15°C and above. Vary dosage according to gas tightness O3f building. Also use lower dosage for larger spaces over 14 000 m^3 (500 000ft^3). The use of a procedure for gas analysis, e.g. thermal conductivity analyser, is recommended so that c x t products can be determined and the required treatment conditions assured.

(b) Hydrogen cyanide (HCN)

8 to 12g/m^3 for 24 h at 15°C and above. If building is thoroughly cleaned inside to remove accumulations of debris, a lower dosage may be used.

(c) Chloropicrin

16g/m^3 for 24 h at 15°C and above. In view of strong tear gas effect it is not recommended for large structures. It may be atomized at lower temperatures by aerosols (see text).

(d) Dichlorvos (DDVP)

Dichlorvos vapour applied with treatments given below is effective against insects moving freely on surfaces or in the free space of closed structures, but it does not penetrate effectively into deep cracks and crevices (see text for full discussion).

Tobacco warehouses. Dispensed more conveniently as an aerosol, but may be applied as a spray.

Cigarette beetle, Lasioderma serricorne (F.):71 mg/m^3 (2 9/l 000 ft^3) twice a week (Tenhet et al, 1958; Childs, et al, 1966). An effective programme for year-round control of this insect is one HCN fumigation per year at 48g/m^3 (48 oz/l 000 ft^3) for 72 h together with dichlorvos 71 mg/m^3 (2 9/1 000 ft^3) twice a week (Childs, 1967).

Tobacco moth, Ephestia elutella (Hbn.): 35 mg/m³ (1 g/l 000 ft³) per week (Press and Childs, 1966).

Stored-product insects generally. In warehouses, mills and other structures, dichlorvos in vapour form is effective against some of these insects (Attfield and Webster, 1966). Use in the presence of foodstuffs would be contingent upon official government approval for residue tolerances and public safety.

Houses, aeroplanes and buildings generally. For public health. Control of flies, mosquitoes, cockroaches, bedbugs, etc.

Dichlorvos dispensed from aerosols or sprays or volatilized from resin strips is now widely used in this field. The literature is extensive. Consult manufacturers' recommendations and regulations of official public health agencies. A comprehensive summary on dichlorvos is given by Attfield and Webster (1966).

N.B. Vapour saturation of dichlorvos occurs at low concentrations. See Table "Properties of dichlorvos" in text.

2. BUILDINGS UNDER GAS PROOF SHEETS

For eradication of residual populations of stored product insects and similar pests.

Methyl bromide

80g/m³ for 24 to 36 h at 0 to 4°C;72g/m³ for 24 to 36 h at 5 to 9°C;64g/m³ for 24 to 36 h at 10 to 14°C or 56g/m³ for 24 to 36 h at 15°C and above. Use of thermal conductivity analyser recommended to check concentrations so that a certain predetermined c x t product may be attained (see text). Additional dosage required for beetles of Troqoderma sp., see Armitage (1956, 1958).

3. HOUSES AND BUILDINGS UNDER GAS PROOF SHEETS OR PROPERLY SEALED AT ALL OUTSIDE POINTS

For dry wood termites (Kalotermes spp.) and other structural wood infesting insects. Coleopterous families Anobiidae, Lyctidae, Bostrichidae, Buprestidae, Cerambycidae, Scolytidae, etc. Hymenopterous species also, including carpenter ants and wood wasps.

(a) Methyl bromide

64g/m³ for 16 to 24 h at 10 to 14°C; or 48g/m³ for 16 to 24 h at 15°C and above. Exposure period may be reduced at temperatures above 20°C. Use of thermal conductivity analyser recommended.

(b) Hydrogen cyanide (HCN)

40g/m^3 for 48 h at 10°C and above. Ensure that electrical sparks or pilot flames do not start fire or explosion when high concentrations are localized at start of fumigation.

(c) Sulphuryl fluoride

32g/m^3 for 24 h at 10 to 20°C; or 16g/m^3 for 24 h at 20°C and above. The manufacturer of sulphuryl fluoride provides a special chart (Fumiguide) which, when used in conjunction with a thermal conductivity analyses or other gas analysis technique ensures that fumigant concentrations are being maintained at the desired level (Stewart, 1966).

(d) Acrylonitrile/methylene chloride mixture

This mixture (34 to 66 by volume) has been tested successfully in Florida for dry wood termite control in buildings (Young, 1967). Suggested dosage 64 to 96g/m^3 for 24 h at temperatures above 15°C.

4. EMPTY CARGO SPACES IN SHIPS, EMPTY RAILWAY CARS, ETC.

For residual populations of insects. Proper aeration of cargo spaces in ships after fumigation most important (see text) (Monro, 1969; Monro et al, 1952).

(a) Hydrogen cyanide (HCN)

12g/m^3 for 10 to 12 h at 0 to 4°C; 10g/m^3 for 10 to 12 h at 5 to 9°C or 8g/m^3 for 10 to 12 h at 10°C and above.

(b) Methyl bromide

32g/m^3 for 10 to 12 h at 0 to 4°C; 24g/m^3 for 10 to 12 h at 5 to 9°C or 16g/m^3 for 10 to 12 h at 10°C and above.

Multiply this schedule by 6 for Khapra beetle, Tronoderma qranarium Everts, which is difficult to kill with methyl bromide.

5. SNAILS IN CARGO SPACES AND ON CARGO – See schedule T.

SCHEDULE R. LOCAL (SPOT) FUMIGANTS FOR MILLS

Representative formulations (all parts by volume)

Acrylonitrile 1 : carbon tetrachloride 2
Ethylene dibromide 1 : ethylene dichloride 1 : carbon tetrachloride 3
Ethylene dichloride 3 : carbon tetrachloride 1 (use twice dosage recommended below)
Chloropicrin alone (for most purposes, use 75 percent of dosage recommended below)

Ethylene dibromide 7 : methyl dibromide 3 (weight to weight) (use 33 percent of dosage recommended below).

See Chapter 7 for discussion of fumigant mixtures.

Fumigation should normally only be done when the building is empty of people other than properly trained fumigators (nights, holidays or weekends).

EXPOSURE PERIOD 16 TO 24 HOURS

MILL UNIT	POINT OF APPLICATION	SUGGESTED DOSAGE		
		CUBIC CENTIMETRES OUNCES (MILLILITRES)	FLUID OUNCES (BR.)	FLUID (U.S.)
Elevator boots (each)	Nearest opening in spout to boot, or hole drilled in boot	150	5	6
Reel and purifier conveyors (each)	Pour along entire length	150	5	6
Reel inspouts	Into spout above	150	5	6
Conveyors	At convenient points along entire length	150 per metre	2 per linear foot	2 per linear foot
Sifter sections (each)	Hand hole in spout above each section	150	5	6
Dusters (bran and shorts)	Hand hole at top	300	10	12
Purifier inspouts	Into spout above purifier	150	5	6
Bins (when empty or almost empty)	Splash on walls near top	50 per m	5 per $100ft^3$	6 per $100ft^3$
Rolls – on each side	Into spouts above rolls	150	5	6

SCHEDULE S. FUMIGATION OF SEEDS

A number of fumigants may be used for the fumigation of seeds without affecting subsequent germination and growth. However, seed treatments must be conducted carefully. Important points to consider are:

(a) strict adherence to recommended dosages and exposure periods;
(b) avoidance of excessive temperatures;
(c) thorough aeration of the seeds immediately the required period of exposure has been completed.

Repetition of fumigation with methyl bromide should be avoided. The moisture content of the seeds is a critical factor in many instances, especially when methyl bromide is used; the limitations on moisture content are mentioned in the following schedules whenever applicable.

The effect of the more important individual fumigants on seed germination is discussed in Chapter 6. For general reviews on the subject of seed fumigation see King et al (1960), Lindgren end Vincent (1962) and Parkin (1963).

All the following schedules refer to seed in permeable teens and sacks. Bulk fumigation of seed would present special problems.

A. SEEDS OF ALL SPECIES

Great care must be taken to ensure that the seed is dry (at or below normal moisture content for prolonged storage, usually less than 12 percent).

(a) Hydrogen cyanide (HCN)

Under atmospheric pressure: 40g/m³ for 24h at 10 to 19°C; or 32g/m³ for 24 h at 20°C and above. Under sustained vacuum: 40g/m³ for 3 h at 20°C and above.

Do not fumigate at temperatures below 10°C. It is better to fumigate at 15°C or above. Do not fumigate seed with moisture content above 14 percent. For fumigation of conifers see Richardson and Roth (1968).

(b) Ethylene dichloride/carbon tetrachloride mixture (3:1)

Under atmospheric pressure: 480g/m³ for 24 h at 20°C and above.

(c) Methyl bromide

Under atmospheric pressure: 24g/m³ for 24 h at 10 to 19°C; or 16g/m³ for 24 h at 20°C and above. Under sustained vacuum: 40g/m³ for 3 h at 20°C and above.

Especially important that the seed is dry. Repetition of fumigation should be avoided (see text). Fumigation above 25°C not advisable.

(d) Carbon disulphide

Under atmospheric pressure: 160g/m³ for 24 h at 20°C and above. Highly flammable.

(e) Phosphine

Phosphine may be used to fumigate a wide range of seeds without impairment of germination. The following schedule should be satisfactory for seed fumigation. 2.5 9 of phosphine (generated by application of an aluminium or magnesium phosphide formulation) per m3.

Period of fumigation should be 7 days at 12 to 15°C, 6 days at 16 to 20°C, 5 days at 21 to 25°C or 4 days at 26°C or above. For cottonseed see Schedule P. pare D2.

B. STEM AND BULB EELWORM (Ditvlenchus dipsachi)

Recommendations based on findings of Goodey (1945) and of Lubatti and Smith (1948).

1. SEED OF LUCERNE (ALFALFA)

Methyl bromide

Under atmospheric pressure: 24 h at 12 to 25°C, dosage according to following table of suggested c x t products and moisture content of seed:

MOISTURE CONTENT (PERCENT)	CONCENTRATION X TIME PRODUCT (MG H/L)
Less than 10	1 400 – 1 500
10 – 11	1 200 – 1 300
11 – 12	1 000 – 1 100
12 – 14	800 – 900

Treatment above 14 percent moisture content is not recommended.

2. ONION SEED

<u>Methyl bromide</u>

Under atmospheric pressure: 24 h at 10 to 20°C, dosage according to following table of suggested c x t products and moisture content of seed:

MOISTURE CONTENT (PERCENT)	CONCENTRATION X TIME PRODUCT (MG H/L)
10 – 11	1 000
11 – 12	900
12	800

Treatment above 12 percent moisture content is not recommended.

SCHEDULE T. FUMIGATION FOR CONTROLLING RODENTS AND OTHER MAMMALIAN PESTS, SNAKES, BIRDS, SNAILS, ANTS' NESTS, WASPS AND TERMITES

1. RATS AND MICE IN EMPTY STORAGES AND WAREHOUSES

(a) Hydrogen cyanide (HCN)

To be applied as liquid or from discs. 4°C or above. 2 to 4g/m³ (2 to 4 oz/l 000 ft³) for 6 h.

(b) Methyl bromide

0°C or above; 4g/m³ for 5 h.

(c) Chloropicrin

4°C or above; 8g/m³ from 8 to 12 h.

2. RATS AND MICE IN FRUIT STORAGES AND SPACES CONTAINING FOOD

<u>Methyl bromide</u>

1°C or above; 4g/m³ for 4 h. At this c x t methyl bromide does not normally injure susceptible apples and fruit in storage.

3. RATS AND MICE IN SHIP HOLDS, PREFERABLY WHEN EMPTY

(a) Hydrogen cyanide (HCN)

4°C or above; 2 to 4g/m³ for 2 h. To be applied as liquid or from discs.

(b) Methyl bromide

0°C or above; 4g/m³ for 4 h.

4. RATS, RABBITS AND SNAKES IN GARBAGE AND RUBBISH DUMPS, BURROWS IN FIELDS AND OTHER HARBOURAGES

(a) Hydrogen cyanide (HCN) from calcium cyanide

Calcium cyanide dust is blown by special duster into one hole, and all others from which dust is seen to emerge are plugged. 1°C or above.

(b) Phosphine

Add tablets containing aluminium or magnesium phosphide to the burrow, pack opening with crumpled newspaper and seal tightly by shovelling soil over the entrance. Treat re-opened burrows one or two days after the initial treatment. Special restrictions on the use of this material are made in some countries to protect endangered species of wildlife. All instructions given on the label should be carefully followed.

5. MOLES, WOODCHUCKS, GROUND SQUIRRELS OR PRAIRIE DOGS IN BURROWS, RUNWAYS OR COLONIES

(a) Hydrogen cyanide (HCN)

About 50 9 calcium cyanide per burrow at 1°C or above.

(b) Methyl bromide

10 ml per burrow. A complete mole runway system should be treated in one operation by making openings every 75 to 150 mm (3 to 6 in) along the system and blowing calcium cyanide dust or injecting methyl bromide, closing each hole after application.

(c) Phosphine

See 4 (b) above.

6. ANTHILLS AND NESTS, TERMITE MOUNDS AND COLONIES, AND WASP AND HORNETS' NESTS

(a) Hydrogen cyanide (HCN) from calcium cyanide

Drop small amounts into nests from spoons or, in larger colonies, blow from dusters. 10°C or above.

(b) Carbon disulphide

Pour into nests or colonies. 10°C or above. Do not apply when ground is too dry because fumigant diffuses away rapidly.

7. SNAILS IN CARGO AND IN CARGO SPACES OF SHIPS

Foreign species of snails of medical or agricultural importance may be found in imported cargoes especially military material which may have been left standing outdoors before shipment. Residual populations may be found in the cargo spaces. These snails may be in a condition of aestivation and therefore very difficult to kill. The problem and methods of control by fumigation are fully discussed by Richardson and Roth (1963 and 1965). The identification and economic significance of snails likely to be accidentally imported into the United States are discussed by Burch (1960).

Treatments at atmospheric pressure may be conducted under gas-proof sheets or in shipping sheds, warehouses etc. as long as lethal concentrations are sustained. Under these conditions a continuous check must be kept by means of the thermal conductivity analyser or other suitable analytical method.

The following treatments are essentially summaries of those contained in USDA (1976). The species of snails listed are those usually found under the conditions described above.

Achatina fulica

(a) Methyl bromide at atmospheric pressure: 128g/m^3 for 24 h at 12°C and above.

65g/m^3 minimum concentration at 2 - 12 h.
35g/m^3 minimum concentration at 12 - 24 h.

(b) Hydrogen cyanide (HCN) at atmospheric pressure: 48g/m^3 at 12°C and above.

(c) Ethylene oxide/carbon dioxide 1:9 for 24 h at 12°C and above.

145g/m^3 minimum concentration at 2 - 4 h.
135g/m^3 minimum concentration at 4 - 24 h.

Cochlicella and Hellicella spp.

Methyl bromide at atmospheric pressure: 128g/m^3 for 72 h at 12°C and above.
95g/m^3 minimum concentration within 30 min.
40g/m^3 minimum concentration within 48 to 72 h.

Theba pisana

(a) Methyl bromide at atmospheric pressure: 96g/m^3 for 10 h at 27°C and above and for 16 h at 13 to 26 C.

70g/m³ minimum concentration for first 30 min.
40g/m³ minimum concentration for 30 min to the end.

This schedule can also be used for Helix spp., Otala spp. and Succinea horticola.

(b) Hydrogen cyanide (HCN)

24g/m³ for 24 h at 18°C and above.

Vacuum fumigation of miscellaneous cargo

Methyl bromide in 100 mm Hg pressure sustained vacuum.

(a) Cochlicella and Helicella spp: 128g/m³ for 16 h at 21°C and above.

(b) Theba pisano: 96g/m³ for 6 h at 21°C and above.

APPENDICES

EFFICIENT UTILIZATION OF FUMIGATION SHEETING

Bowen (1961) has published tables giving the dimensions of stacks of goods for maximum volume under gas-proof sheets of various shapes and sizes. As Bowen points out, efficient stacking may permit maximum utilization of available sheets and use of only one rather than two or more fumigations of a given load. He also emphasizes the following points.

1. The square is the best shape for the sheet if the highest ratio of stack volume to sheet is to be achieved. In joining sheets together, therefore, the combination should be as nearly square as possible.

2. The base of the ideal stack will resemble the shape of the sheet used to cover it.

3. Large sheets are more efficient because of the surface to volume relationship.

In the two tables, given here in abbreviated form, the dimensions in feet and metres are calculated from the formula derived by Bowen as follows:

The formula derived for computing the height h of stack for maximum volume under the sheet is,

$$h = \frac{L + W - \sqrt{L(L - w) + W^2}}{6} \quad (1)$$

in which L and W are the effective length and width of the sheet, i.e. the length and width after deducting the overlap at the bottom for sealing. The length 1 and the width w of the ideal stack are then determined by the following relationships:

l = L - 2h (2)

w = W - 2h (3)

If the length and width of the sheet are equal, it becomes a square with effective side A = L = W. Equation (1) for h then reduces to, h = A (4)

and the base of the stack of maximum volume that can be covered by the sheet will also be a square with side a such that,

a = A - 2h = (2A)/3 (5)

Dimensions of stack in metres for maximum volume under square sheets of various sizes allowing for 1-metre overlap (margin) at base of stack

SHEETS[1]		STACK DIMENSIONS FOR MAXIMUM VOLUME			MAXIMUM VOLUME
ACTUAL W X L	EFFECTIVE W X L	HEIGHT	WIDTH	LENGTH	
Metres					Cubic metres
8 x 8	6 x 6	1	4	4	16.0
10 x 10	8 x 8	1.33	5.33	5.33	37.92
12 x 12	10 x 10	1.67	6.67	6.67	74.06
14 x 14	12 x 12	2.0	8.0	8.0	128.0
15 x 15	13 x 13	2.17	8.67	8.67	162.74
16 x 16	14 x 14	2.33	9.33	9 33	203.25
18 x 18	16 x 16	2.67	10.67	10.67	303.39
20 x 20	18 x 18	3.0	12.0	12.0	432.0

DIMENSIONS OF STACK IN FEET FOR MAXIMUM VOLUME ALLOWING FOR 3-FOOT MARGIN

SHEETS[1]		STACK DIMENSIONS FOR MAXIMUM VOLUME			MAXIMUM VOLUME
ATUAL W X L	EFFECTIVE W X L	HEIGHT	WIDTH	LENGTH	
FEET					CUBIC FEET
25 x 25	19 x 19	3.17	12.67	12.67	509
30 x 30	24 x 24	4.00	16.00	16.00	1 024
35 x 35	29 x 29	4.83	19.34	19.34	1 807
40 x 40	34 x 34	5.67	22.67	22.67	2 914
45 x 45	39 x 39	6.50	26.00	26.00	4 394
50 x 50	46 x 46	7.67	30.67	30.67	7 215

[1]W x L = Width by length

Thanks are extended to M.F. Bowen of Millbrae, California, for permission to reproduce his calculations in abbreviated form.

CONVERSION FACTORS AND RELATIONSHIPS USEFUL IN FUMIGATION WORK

ABBREVIATIONS

avoirdupois	AVDP	kilogram	KG
bushel	BU	kilometre	KM
centimetre	CM	metre	M
cubic centimetre	CM^3	milligram	MG
cubic foot	FT^3	millilitre	ML
cubic inch	IN^3	millimetre	MM
cubic metre	M^3	ounce	OZ
cubic yard	YD^3	pound	LB
fluid	FL	quart	QT
foot	FT	square	SQ
gallon	GAL	square centimetre	CM^2
gram	G	square foot	FT^2
hectare	HA	square inch	IN^2
hundredweight	CWT	square metre	M^2
inch	IN	yard	YD

BRITISH OR UNITED STATES SYSTEMS TO METRIC	METRIC TO BRITISH OR UNITED STATES SYSTEMS
Length	
1 in = 2.540 cm	1 cm = 0.394 in
1 ft = 0.305 m	1 m = 39.37 in
1 yd = 0.914 m	1 m = 3.281 ft
1 mile = 1.609 km	1 m = 1.094
Area	
1 in2 = 6.452 cm^2	1 cm^2 = 0.155 in^2
1 ft2 = 0.093 m^2	1 m^2 = 1 550 in^2
1 yd2 = 0.836 m^2	1 m^2 = 10.764 ft^2
1 acre = 0.405 ha	1 m^2 = 1.196 yd^2
	1 ha = 2.471 acres

Volume

1 in^3 = 16.39 cm^3	1 litre = 61.025 in^3
1 ft^3 = 28.316 litres	1 cm^3 = 0.061 in^3
1 ft^3 = 0.028 m^3	1 m^3 = 35.314 ft^3
1 yd^3 = 764.5 litres	1 m^3 = 1.308 yd^3
1 yd^3 = 0.764 m^3	1 m^3 = 27.496 bu (Br)
1 000ft^3 = 28.31 m^3	1 m3 = 28.377 bu (U.S.)
1 bu (Br) = 36.368 litres	1 litre = 0.0275 bu (Br)
1 bu (U.S.) = 35.238 litres	1 litre = 0.0284 bu (U.S.)
1 000 bu (Br) = 36.37 m^3 =1 284 ft^3	
1 000 bu (U.S.) = 35.24 m^3 =1 244 ft^3	

British and United States volumes

1 bu (Br) = 1.032 bu (U.S.)
1 bu (U.S.) = 0.969 bu (Br)
1 bu (Br) = 1.284 ft^3
1 bu (U.S.) = 1.244 ft^3

Liquid measure

1 fl Br oz = 28.41 ml	1 litre = 35.196 Br fl oz
1 fl U.S. oz = 29.57 ml	1 litre = 33.815 U.S. fl oz
	1 litre = 0.88 Br qt
1 Br pint = 568.2 ml	1 litre = 1.06 U.S. qt
1 U.S. Pint = 473.2 ml	1 litre = 1.76 Br pints
	1 litre = 2.11 U.S. pints
1 Br gal = 4.546 litres	1 litre = 0.22 Br gal
1 U.S. gal = 3.785 litres	1 litre = 0.26 U.S. gal

British and United States liquid measure

1 Br pint = 1.201 U.S. pints
1 Br qt = 1.201 U.S. qt
1 Br gal = 1.201 U.S. gal
1 U.S. gal = 0.833 Br gal
1 Br gal = 4 qt = 8 pints = 160 fl oz

1 U.S. gal = 4 qt = 8 pints = 128 fl oz
1 Br gal = 0.161 ft^3
1 U.S. gal = 0.134 ft^3

Weight

1 oz = 28.35 g	1 g = 0.035 oz
1 lb = 453.59 9	1 kg = 35.27 oz
1 lb = 0.454kg	1 kg = 2.205 lb
1 long cwt = 112 lb	1 quintal (metric) = 100 kg
1 long cwt = 50.8 kg	1 quintal (metric) = 1.9684 long cwt
20 long cwt = 1 long ton	1 quintal (metric) = 220.46 lb
20 long cwt = 2 240 lb	1 quintal (metric) = 2.2046 short cwt
1 short cwt = 100 lb	10 quintals (metric) = 1 metric tonne
1 short cwt = 45.36 kg	10 quintals (metric) = 0.9842 long ton
20 short cwt = 1 short ton	10 quintals (metric) = 1.1023 short tons
20 short cwt = 2 000 lb	
1 long ton = 1.016 metric tonnes	1 metric tonne = 0.9842 long ton
1 long ton = 1 016.4 kg	1 metric tonne = 1.1023 short tons
1 short ton = 0.9072 metric tonne	1 metric tonne = 22.046 short cwt
1 short ton = 907.2 kg	1 metric tonne = 19.684 long cwt

Fulminant dosage relationships

oz/1 000 ft^3 =g/m^3 = mg/litre (approximately)

OTHER CONVERSION FACTORS

Under practical conditions, use same figure for pounds per 1 000 bushels U.S. or Br (1 lb/1 000 U.S. bu = 1 032 lb/1 000 Br bu).

U.S. gal/1 000 U.S. bu to Br gal/1 000 Br bu x 0.86 (0.9 approximately)
Br gal/1 000 Br bu to U.S. gal/1 000 U.S. bu x 1.16
lb/1 000 Br bu tog/m^3 x 12.47
lb/1 000 U.S. bu tog/m^3 x 12.87
Br gal/1 000 Br bu to litre/m^3 x 0.125
U.S. gal/1 000 U.S. bu to litre/m^3 x 0.107
Br gal/1 000 ft^3 to litre/m^3 x 0.161
U.S. gal/1 000 ft^3 to litre/m^3 x 0.134

GRAIN STOWAGE

<u>Wheat</u>

60 lb/bu; 48.25 lb/ft^3
37.33 bu/long ton; 33.73 bu/short ton
1 long ton stows in 46.4 ft^3; 1 short ton in 41.45 ft^3
1 long ton stows in 1.3 m^3; 1 short ton in 1.17 m^3
1 000 bu = 26.8 long tons = 30 short tons = 27.2 metric tonnes

<u>Barley</u>

48 lb/bu; 38.6 lb/ft^3
46.66 bu/long ton; 41.67 bu/short ton
1 long ton stows in 58 ft^3; 1 short ton in 51.8 ft^3
1 long ton stows in 1.6 m3; 1 short ton in 1.5 m^3
1 000 bu = 21.4 long tons = 24 short tons = 21.8 metric tonnes

<u>Maize, shelled</u>

56 lb/bu; 45 lb/ft^3
40 bu/long ton; 35.7 bu/short ton
1 long ton stows in 50 ft^3; 1 short ton in 44.5 ft^3
1 long ton stows in 1.5 m3; 1 short ton in 1.01 m^3
1 000 bu = 25 long tons = 28 short tons = 25.4 metric tonnes

TEMPERATURE

Degrees Centigrade (°C) to degrees Fahrenheit = (°C x 1.8) + 32
Degrees Fahrenheit(°F) to degrees Centigrade = (°F – 32) x 0.55 (or x 5/9)

REPRESENTATIVE CONVERSIONS

°C	−17.8	−10	0	5	10	15	20	25	30	32.2	35
°F	0	14	32	41	50	59	68	77	86	90	95

DECREES CENTIGRADE INTO DECREES FAHRENHEIT

CENTIGRADE	0	1	2	3	4	5	6	7	8	9
−40	−40.0									
−30	−22.0	−23.8	−25.6	−27.4	−29.2	−31.0	−32.8	−34.6	−36.4	−38.2
−20	− 4.0	− 5.8	− 7.6	− 9.4	−11.2	−13.0	−14.8	−16.6	−18.4	−20.2
−10	+14.0	+12.2	+10.4	+ 8.6	+ 6.8	+ 5.0	+ 3.2	+ 1.4	− 0.4	− 2.2
0−	+32.0	+30.2	+28.4	+26.6	+24.8	+23.0	+21.2	+19.4	+17.6	+15.8
0+	+32.0	+33.8	+35.6	+37.4	+39.2	+41.0	+42.8	+44.6	+46.4	+48.2
10	50.0	51.8	53.6	55.4	57.2	59.0	60.8	62.6	64.4	66.2
20	68.0	69.8	71.6	73.4	75.2	77.0	78.8	80.6	82.4	84.2
30	86.0	87.8	89.6	91.4	93.2	95.0	96.8	98.6	100.4	102.2
40	104.0	105.8	107.6	109.4	111.2	113.0	114.8	116.6	118.4	120.2
50	122.0	123.8	125.6	127.4	129.2	131.0	132.8	134.6	136.4	138.2

60	140.0	141.8	143.6	145.4	147.2	149.0	150.8	152.6	154.4	156.2
70	158.0	159.8	161.6	163.4	165.2	167.0	168.8	170.6	172.4	174.2
80	176.0	177.8	179.6	181.4	183.2	185.0	186.8	188.6	190.4	192.2
90	194.0	195.8	197.6	199.4	201.2	203.0	204.8	206.6	208.4	210.2

DEGREES FAHRENHEIT INTO DEGREES CENTIGRADE

FAHREN HEIT	0	1	2	3	4	5	6	7	8	9
0	–17.8	–17.2	–16.7	–16.1	–15.6	–15.0	–14.4	–13.9	–13.3	–12.8
10	–12.2	–11.7	–11.1	–10.6	–10.0	– 9.4	– 8.9	– 8.3	– 7.8	– 7.2
20	– 6.7	– 6.1	– 5.6	– 5.0	– 4.4	– 3.9	– 3.3	– 2.8	– 2.2	– 1.7
30	– 1.1	– 0.6	0	+ 0.6	+ 1.1	+ 1.7	+ 2.2	+ 2.8	+ 3.3	+ 3.9
40	4.4	5.0	5.6	6.1	6.7	7.2	7.8	8.3	8.9	9.4
50	10.0	10.6	11.1	11.7	12.2	12.8	13.3	13.9	14.4	15.0
60	15.6	16.1	16.7	17.2	17.8	18.3	18.9	19.4	20.0	20.6
70	21.1	21.7	22.2	22.8	23.3	23.9	24.4	25.0	25.6	26.1
80	26.7	27.2	27.8	28.3	28.9	29.4	30.0	30.6	31.1	31.7
90	32.2	32.8	33.3	33.9	34.4	35.0	35.6	36.1	36.7	37.2
100	37.8	38.3	38.9	39.4	40.0	40.6	41.1	41.7	42.2	42.8

110	43.3	43.9	44.4	45.0	45.6	46.1	46.7	47.2	47.8	48.3
120	48.9	49.4	50.0	50.6	51.1	51.7	52.2	52.8	53.3	53.9
130	54.4	55.0	55.6	56.1	56.7	57.2	57.8	58.3	58.9	59.4
140	60.0	60.6	61.1	61.7	62.2	62.8	63.3	63.9	64.4	65.0
150	65.6	66.1	66.7	67.2	67.8	68.3	68.9	69.4	70.0	70.6
160	71.1	71.7	72.2	72.8	73.3	73.9	74.4	75.0	75.6	76.1
170	76.7	77.2	77.8	78.3	78.9	79.4	80.0	80.6	81.1	81.7
180	82.2	82.8	83.3	83.9	84.4	85.0	85.6	86.1	86.7	87.2
190	87.8	88.3	88.9	89.4	90.0	90.6	91.1	91.7	92.2	92.8
200	93.3	93.9	94.4	95.0	95.6	96.1	96.7	97.2	97.8	98.3
210	98.9	99.4	100.0							

GENERAL FIRST AID FOR ACCIDENTS WITH FUMIGANTS

Detailed instructions for first aid for accidents with hydrogen cyanide (HCN) methyl bromide, phosphine and dichlorvos are given in Chapter 6, under the heading of each of these fumigants. The following more general instructions apply to accidents from inhalation or spilling of poisonous chemicals and are suggested for chemicals in common use. These instructions are taken from the pertinent sections of the recommendations for first aid for poisoning by courtesy of the publisher, the Committee on Toxicology of the American Medical Association.

FIRST AID MEASURES FOR POISONING

First aid must be started at once. If possible, one person should begin treatment while another calls a physician. When this is not possible, the nature of the poison will determine whether to call a physician first or begin first aid measures and then notify a physician.

Measures to be taken before arrival of a physician

Inhaled poisons

1. Carry patient (do not let him walk) to fresh air immediately.
2. Open all doors and windows.
3. Loosen all tight clothing.
4. Apply artificial respiration if breathing has stopped or is irregular.
5. Prevent chilling (wrap patient in blankets).
6. Keep patient as quiet as possible.
7. If patient is convulsing, keep him in bed in semi dark room; avoid jarring or noise.
8. Do not give alcohol in any form.

Skin contamination

1. Drench skin with water (shower, hose, faucet).
2. Apply stream of water on skin while removing clothing.
3. Cleanse skin thoroughly with water; rapidity in washing is most important in reducing extent of injury.

Eve contamination

1. Hold eyelids open, wash eyes with gentle stream of running water immediately. Delay of a few seconds increases extent of injury.
2. Continue washing until physician arrives.
3. Do not use chemicals; they may increase extent of injury.

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