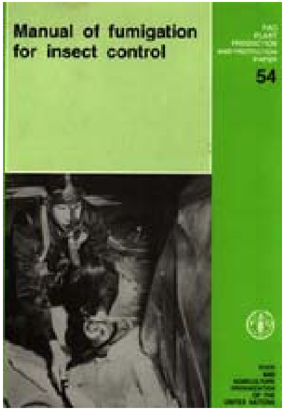

Manual of fumigation for insect control

Table of contents

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Contents

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4. Field determination of fumigants

5. Fumigant residues

6. Chemicals used as fumigants

7. Fumigant mixtures

8. Space fumigation at atmospheric pressure

9. Vacuum fumigation

Appendices

Home"" """"> ar.cn.de.en.es.fr.id.it.ph.po.ru.sw

Acknowledgments

Contents - Next

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This publication is based on the Manual of fumigation for insect control (FAO Agricultural Studies No. 79, FAO Plant Production and Protection Series No. 20), by H.A.U. Monro, which first appeared in 1961 and was reprinted in 1964. A second edition, revised by the author, was published in 1969 and was reprinted five times.

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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 need 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 pesticidal 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 affored 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 reproduced by kind permission of the Slough Laboratory, Ministry of Agriculture, Fisheries and Food, UK.

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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.

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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.

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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 defintion 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.

Contents - **Next**

Home"" """"> ar.cn.de.en.es.fr.id.it.ph.po.ru.sw

Evaporation of fumigants

Contents - Previous - Next

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 volatilzation 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 (20C to 25C). 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 volatilzed. 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 25C	3-17
Carbon disulphide CS_2	76.13	46.3	0.22 at 22C	1.25-44
Carbon tetrachloride	153.84	77.0	0.08 at 20C	Nonflammable

CCl_4				
Chloropicrin $CCl_3.NO_2$	164.39	112.0	Insoluble at20C	Nonflammable
Dichlorvos (DDVP) CCl_2=CHO.Po.$(OCH_3)_2$	221	120C/14mm	Slight	Nonflammable
Ethylene dibromide $CH_2Br.CH_2Br$	187.88	131.0	0.43 at 30C	Nonflammable
Ethylene dichloride $CH_2Cl.CH_2Cl$	98.97	83.0	**0.87 at 20C	6-16
Ethylene oxide $CH_2.O.CH_2$	44.05	10.7	Very soluble at 20C	3-80
Ethyl formate H.COO C_2H_5	74.05	**54.0	**11.8 at 25C	2.7 - 13.5
Hydrogen cyanide HCN	27.03	26.0	Very soluble at 20C	6-41
Methyl bromide CH_3Br	94.95	3.6	1.3 at 25C	Nonflammable
Methyl formate H.COO	60.03	**31.0	**30.4	5.9 - 20

CH_3				
Paradichlorobenzene $C_2H_4Cl_2$	147.01	173.0	0.008 at 25C	(Flash point***
Phosphine PH_3	34.04	**-87.4	**Very slightly soluble	1.79
Sulphuryl fluoride SO_2F_2	102.6	-55.2	Slight	Nonflammable
Trichloroethylene CHCl : CCl_2	131.4	86.7	**Insoluble	Nonflammable

*** Unless other reference given, boiling point and solubility data are from Martin (1961) and flammably 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 nonflammable 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.

Nonflammable 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							

	0C (32F)	**5C** (41F)	**10C** (50F)	**15C** (59F)	**20C** (68F)	**25C** (77F)	**30C** (86F)	**35C** (95F)
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 calculed from formulas derived by Roark and Nelson (1929).-[2] Equivalent to milligrames 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 gramme 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 heavierthan-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).

Phvsical 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 21C (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 131C) and of hydrogen cyanide (boiling point 26C) than of methyl bromide (boiling point 3.6C). (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 humidities 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 4C. Lindgren et al (1962) found an increase in the bromide content of wheat as the temperature during fumigation rose from 10 to 32C.

Contents - Previous - Next

Home"" """"> ar.cn.de.en.es.fr.id.it.ph.po.ru.sw

Significance of residues in foods

Contents - Previous - Next

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 Venetables

(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 grammes per cubic metre (g/m), 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 or oz/1 000ft).

By a fortunate coincidence in units of measurement, grammes 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 milligrammes per litre (mg/l), equivalent to grammes 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 gramme molecular weight of the substance occupies 22.414 litres at 0C 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 grammes per cubic metre (or milligrammes 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.

<u>Example</u>. To convert 1g/m of PH_3 (molecular weight 34 approximately)

(1x22.4)/34	= .659 cmper 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 grammes per cubic metre (or milligrammes 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.

<u>Example</u>. 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 (or mg/l or oz per 1 000 ft)

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 grammes 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 20C, a concentration of 33.2 milligrammes per litre of methyl bromide must be maintained for 5 hours. The product 33.2 milligrammes per litre x 5 hours = 166 milligrammes 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 (milligramme 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 20C and 70 percent relative humidity for various exposures:

TABLE 3. - REQUIRED CONCENTRATION X TIME (c x t) PRODUCTS TO OBTAIN 99 PERCENT MORTALITY OF TENEBROIDES 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 20C.(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 gramme hours per cubic metre (9 h/m), which is equivalent to 190 milligramme hours per litre (mg h/l).

Leakage from the 100 m 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 grammes 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 milligrammes 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 are added to sustain tbe concentration. After 11.7 hours the desired c x t product of 190 9 h/m 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.

Contents - Previous - Next

Home"" """"> ar.cn.de.en.es.fr.id.it.ph.po.ru.sw

Toxicity of fumigants to insects

Contents - ◄Previous - Next►

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 35C, 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 10C, 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 insects 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.

Prefumination and Postfumioation 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 postfumigation 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 farreaching 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 10C. 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 4C.

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 humidities 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 so 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 nonflammable, 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 28C
(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 nontreated 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 25C 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 posttreatment 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 indviduals 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 crossresistance 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.

Contents - Previous - Next

Home"" """"> ar.cn.de.en.es.fr.id.it.ph.po.ru.sw

3. Safety precautions and protective devices

Contents - Previous - Next

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 timeweighted 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 prewarning gas in structures, such as ships, where stowaways may be concealed, or in large buildings that are difficult to inspect completely. The prewarming gas is applied separately between 15 to 30 minutes in advance of the main fumigant. A dosage recommended for chloropicrin

as a prewarning gas is 6 g/100m (1 oz/15 000 ft). 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	**TLV**	
		TWA	**STEL**

	threshold		
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 Industria 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 industrialtype 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 facepiece, 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	
l,l,l - 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 facepiece, 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 or oz/l 000 ft).

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 facepiece by a hose, pinch the hose off tightly with the hand. If the facepiece 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).

Contents - Previous - Next

Home"" """"> ar.cn.de.en.es.fr.id.it.ph.po.ru.sw

Detection of fumigants

Contents - Previous - Next

The importance of having proper equipment for detection of fumigants (down to the threshold limits) cannot be overemphasized. Needless accidents have occured 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 priciples 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 handoperated 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 30C 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.**

<u>Halide Leak Detector</u>

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

micronsize 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
Phosphine3	10.1	1.0	1,000	

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

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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 largescale 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 opticallyworked 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 dilutionsampling 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.

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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):

<u>Residue</u>: 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.

<u>Food factor</u>: 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.

<u>Acceptable daily intake</u>: 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 milligrammes of the chemical, as it appears in the food, per kilogramme 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.

Contents - Previous - Next

Home"" """"> ar.cn.de.en.es.fr.id.it.ph.po.ru.sw

Factors affecting residue accumulation

Contents - Previous - Next

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 humidities (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 witholding 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.

Contents - Previous - Next

Home"" """"> ar.cn.de.en.es.fr.id.it.ph.po.ru.sw

Methyl bromide

Contents - Previous - Next

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 microorganisms 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 nonflammable 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	3.6C (38.5F)
Freezing point	-93C
Molecular weight	94.95
Specific gravity gas (air=1)	3.27 at 0C
liquid (water at 4C=1)	1.732 at 0C
Latent heat of vaporization	61.52 cal/g
Flammability limits in air	Nonflammable (see next page)
Solubility in water	1.34 g/100 ml at 25C
Pertinent chemical properties	Powerful solvent of organic materials, especially natural

	rubber. When pure, noncorrosive to metals. Liquid reacts with aluminium (see text)
Method of evolution as fumigant	From steel cylinders under naturalor added pressure. Also dispensed from 1 lb cans or 20 ml glass ampoules
Commercial purity	99.4%

Natural vapour pressure at different temperatures

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

Weights and volumes of liquid

1 lb (avdp) at 0C 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 (25C and 760 mm pressure)

By volume		Weight per volume	
Parts per million	**Percent**	**[1]g/m**	**lb/1000 ft**
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 milligrammes per litre

Treatments of a wide range of commodities may be conducted at temperatures down to

4c, 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 nonflammable when ignition is attempted with a flame.

Simmons and Wolfhard (1955) also confirmed that mixtures of methyl bromide and air are nonflammable. 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 20C 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 18C and 10, 13 and 16 percent moisture content) and he concluded that, although the lower values of dosage, temperature amd 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 - 30C 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 posttreatment 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 30C, were not always injured. Breakdown of cured sweet potatoes after fumigation was associated with postfumigation storage temperatures. Material held at 21 to 27C 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. Occurence 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 naterials 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 I lows, cushions and mattresees;**

- **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 260C).

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 ly 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 merdicinal dose of bromide salt (Phi I I ips 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 unrousted 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.

Continue

Contents - Previous - Next

Evaluation of Residues

Contents - Previous - Next

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 alchohol. 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.

<u>Care and operation of lamps</u>. 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 chrometopraphy. 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.

<u>Chemical analysis</u>. 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) 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 nalysis of insecticides (Jacobs, 1949; Gunther and Blinn, 1955).

<u>Other field methods</u>. 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 g 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 hydrolyzed 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 (3.6C). If the can is immersed in a pail of hot water (not above 77C), 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 15C 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.

<u>Evaporating pans</u> 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 15C, the pan may be warmed in some way, preferably with heating coils, infra-red heaters or ordinary light bulbs.

<u>Precautions in discharge</u> Although methyl bromide is nonflammable, 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 0C). 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 (5 lb/1000 ft) 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 FUMIGATION(CANISTER OF THE TYPE USED I-OR ORGANIC VAPOURS)*

Concentration of methyl bromide g/m (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 occlu sive 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 embarassment 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.

Contents - Previous - Next

Home"" """"> ar.cn.de.en.es.fr.id.it.ph.po.ru.sw

Phosphine

Contents - Previous - Next

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.

$$AlP + 3H_2O \; PH_3{}^\wedge + Al(OH)_3$$

$$Mg_3P_2 + 6H_2O \; 2PH_3{}^\wedge + 3Mg(OH)_2$$

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 greywrlite 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	-87.4C
Freezing point	-133.5C
Molecular weight	34.04
Specific gravity gas (air = 1)	1.214
liquid (water at 4C = 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 17C (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

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

Dosages and concentrations of gas in air (25C and 760 mm pressure)

By volume		Weight per volume	
Parts per million	**Percent**	**^{1}g/m**	**lb/l 000ft**
20.3	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 milligrammes 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 5C, so that longer exposure times are required for it to exert its effect. It is not recommended for use below 5C. 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 storedproduct 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 m or at 9.0 m unless carbon dioxide is present; carbon dioxide interferes with analysis of phosphine at 4.2 m and may need to be absorbed from the sample or the analysis may be done at 9.0 m. 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 moisturepermeable 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 phytotoxicity.

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 phopshide 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 prepack 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 eighthour 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 alcholic 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 applicaion 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), unconciousness 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 (hoematuria, 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 haemoconcentration, 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.

Contents - Previous - Next

Home"" """"> ar.cn.de.en.es.fr.id.it.ph.po.ru.sw

Hydrogen cyanide (HCN)

Contents - Previous - Next

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	26C
Freezing point	-14C
Molecular weight	27.03
Specific gravity gas (air = 1)	0.9

liquid (water at 4C =1)	0.688 at 20C
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

0C (32F) 264.3 mm Hg
10C (50F) 400.0 mm Hg
20C (68F) 610.0 mm Hg

25C (77F) 738.8 mm Hg
30C (86F) 910.0 mm Hg
40C (104F) 1 269.2 mm Hg

Weights and volumes of liquid

1 lb (avdp) at 20C 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 (25C and 760 mm pressure)

By volume		Weight per volume	
Parts per million	Percent	^{1}g/m	lb/l 000 ft
210	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 milligrammes per litre

[2] Threshold limit (ACGIH, 1981).

Toxicity to Insects

Among the commonly used famigants, HCN is one of the most toxic to insects. It aiso has a rapid paralyzing 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 atteined as quickly as possible during

the application of the fumigant.

FLAMMABILITY

The flammability limits of HCN in air lie botween 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 or 16 oz/l 000 ft). However, it must be pointed out that, at the point of release of the gas at the beginning of a famigation, 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 ageinst 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 postfumigation storage. It wes concluded that germination of wheat, barley, oats, rice and flax seeds wes not impaired by one or two famigations 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 mintues. 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 normel 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 Veqetables

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 ageinst 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 throogh a mass of

grain sorghum. The variables of temperature, moisture and dockage all reduced penetration in proportion to their increase.

Dried Fruit

Althoogh HCN has heen used for many years in the treatment of dried fruit, this practice is safe only under carefully controlled conditions. HCN may react with laevolose to form laevolose cyenohydrin, a poisonous compound that is feirly 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 famigation. 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 hydrocyenic acid present at the time of consumption (American public Health Association, 1938).

METHODS OF ANALYSIS

Determination of Vopours

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.

<u>Test papers</u>. 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 10C. 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 qas 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 photooptic 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 analyzed. 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 eggshaped) 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 dispen ing 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 precool them in cold water, ice, or in a refrigerator at 0C. 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 (oz/1 000 ft)	

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 cmof 3 percent solution);**
- **2 ampoules of sodium thiosulphate (50 cmof 25 percent solution);**
- **1 sterile syringe, 10 cm;**
- **1 sterile syringe, 50 cm;**

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. Canistertype 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 srtifical respiration if breathing has stopped.

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

<u>Suquested Care by a Physician</u>

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 cmof 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 cmper 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 HolgerNielson 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.

Contents - Previous - Next

Home"" """"> ar.cn.de.en.es.fr.id.it.ph.po.ru.sw

Ethylene dibromide

Contents - Previous - Next

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	131.6C
Freezing point	10 C
Molecular weight	187.88
Specific gravity	
gas (air = 1)	6.487
liquid (water at 4C = 1)	2.172 at 20C
Latent heat of vaporization	46.2 cal/g

Flammability limits in air	Nonflammable
Solubility in water	0.431 g/100 ml at 30C
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

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

Weights and volumes of liquid

1 lb (avdp) at 25C 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 (25C and 760 mm pressure)

By volume		Weight per volume	
Parts per million	**Percent**	**g/m**	**lb/l 000 ft**
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 milligrammes 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 27C 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 21.1C) 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.

Venetables

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 occuring 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 witholding

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 13C declined rapidly in the first two days after treatment but required nearly four weeks at 13C to desorb to 0.1 mg/kg (Dumas and Bond, 1975). In studies on grapefruit treated to eliminate possible infestation by larvae of the Coribbean 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 21C.

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 25C.

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 Vepours

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 microdetermination 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.

Determination of Residues

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.

Contents - Previous - Next

Home"" """"> ar.cn.de.en.es.fr.id.it.ph.po.ru.sw

Ethylene oxide

Contents - Previous - Next

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 nonflammable carrier. It is obtainable mixed with carbon dioxide in the proportion of one part ETO to nine parts CO_2 by weight or lt or 12 percent ETO with nonflammable 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	10.7C
Freezing point	-111.3C
Molecular weight	44.05
Specific gravity	
gas (air = 1)	1.521
liquid (water at 4C = 1)	0.887 at 7C
Latent heat of vaporization	139 cal/g
Flammability limits in air	3 to 80% by volume
Solubility in water	Infinite at 0C
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

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

Weights and volumes of liquid

1 lb (avdp) at 7C 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 (25C and 760 mm pressure)

By volume		Weight per volume	
Parts per million	Percent	g/m	lb/l 000 ft
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 milligrammes 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 27C. 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 insectfree 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 25C, 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 technigues 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 CO2. For some applications in specially designed equipment, under expert supervision, there is also available a mixture of 90 percent ETO and 10 percent CO2. 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 25C 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 : CO2) 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 (25 lb/1000 ft) for 12 to 24 hours. The atmosphere in an empty chamber would thus contain 2.2 percent ETO and 19.8 percent CO2. Selfcontained 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 nonflammable 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 a 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	83.5C
Freezing point	-35.3C
Molecular weight	98.97
Specific gravity gas (air = l)	3.42
liquid (water at 4C = 1)	1.257 at 20C
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 20C

Pertinent chemical properties	Flash point 12 to 15C. Stable and noncorrosive
Method of evolution as fumigant	By evaporation of liquid. Always used in mixture with nonflammable fumigant or carrier, such as carbon tetrachloride

Natural vapour pressure at different temperatures

0C (32F)	**23 mm Hg**
10C (50F)	**40 mm Hg**
20C (68F)	**65 mm Hg**
25C (77F)	**81.0 mm Hg**
30C (86F)	**103.0 mm Hg**
40C (104F)	**160.0 mm Hg**

Weights and volumes of liquid

1 lb (avdp) at 20C 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 **(25C and 760 mm pressure)**

By volume		Weight per volume	
Parts per million	**Percent**	**g/m**	**lb/l 000 ft**
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 milligrammes per litre

Wheat treated at 1 l/m (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). 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.

Contents - Previous - Next