# Requirements for Fumigation and Controlled Atmospheres as Options for Pest and Quality Control in Stored Grain

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#### Abstract

Funigation may be thought of as having two roles: one to allow rapid removal of live insects to meet short-term goals, and the other as a preliminary to, or component of, long-term storage. While funigation of grain is primarily for insect control, good control of insects also makes possible the better preservation of other quality parameters. Both funigation and controlled atmospheres, if used correctly, can give a very high level of insect control. Although similar principles apply to the use of both processes, details of adding, distributing and retaining the gases vary. This paper uses a range of well-documented treatments to demonstrate how these general principles have been employed with a variety of gases and storage structures. These show that many enclosures can be used for successful gaseous treatments if an appropriate level of sealing is attained. This level of sealing depends to some extent on the gas distribution and introduction methods. Methods of continuous gas addition are under development. These may allow gaseous treatment in enclosures currently considered impossible to seal economically.

BOTH controlled atmosphere (CA) storage and fumigation are techniques that rely on a gas or a mixture of gases as a means for controlling the effects of biological agents that may cause quality degradation. This paper aims to show that both gaseous processes have much in common and their uses overlap substantially. However, individual controlled atmospheres and fumigants have properties that make them more appropriate for particular roles. The specific details of these properties are discussed elsewhere in these proceedings (Banks 1990; Graver 1990). Here, discussion will be general and aims to identify the role of fumigation and controlled atmospheres as options for pest and quality control, by identifying the agents of quality change and how CA and fumigation may affect them. The general criteria for a successful gaseous treatment, and the consequences of failure to meet them, are considered. Specific discussion on how to ensure success by setting treatment targets gives a background to adapting treatment techniques to meet the targets. A series of examples is presented to show how these targets can be reached in practice and to demonstrate that fumigation and CA are options for pest and quality control in a wide range of storage enclosures.

Controlled atmospheres (CAs) as used in grain storage are mixtures of those gases normally found in the storage atmosphere: nitrogen, oxygen, and carbon dioxide. In CAs, the oxygen concentration is reduced and/or the carbon dioxide concentration increased. Specific CAs are generally named by their means of production, maintenance or active component, and are usually designated as one of the following types of atmosphere: modified, oxygen deficient, low oxygen, carbon dioxide enriched, high carbon dioxide, nitrogen, burner gas and hermetic storage.

CAs have not had extensive usage in modern commercial grain storage, despite hermetic stor-

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age — one of the variants of CA —being one of the methods of grain storage with the longest continuous history of use (Bowen and Wood 1986; Sigaut 1980). Where CAs have been used, they have normally formed part of a disinfestation and physical protection system (Shejbal (1980) gives many examples). In this, the atmosphere controls the quality degrading biological agent and the containing enclosure acts as both a barrier against gaseous interchange and insect reinfestation.

Fumigants, on the other hand, are highly toxic gases (or vapours) unlikely to form a normal part of the storage atmosphere. They are added to the storage specifically to kill a target organism or group of organisms. These organisms are usually, but not always, insects. Over the years, a fairly wide range of compounds has been used as fumigants either singly or in combination. These have included the following: ethylene dichloride, carbon tetrachloride, carbon disulphide, ethylene dibromide, chloropicrin, hydrogen cyanide, ethylene oxide, methyl chloride, methyl bromide, and phosphine. For a variety of reasons, only methyl bromide and phosphine remain in widespread use.

Traditionally, fumigation has been used as a rapid method of killing insects, either to meet a specific requirement such as quarantine, or as part of a continuing program of insect suppression, applied when insect numbers pass some nominal threshold. In these cases, there is no aim for continuous protection. Rather, the aim is to reduce insect damage as much as possible and to market a commodity at a level of infestation acceptable to the market or its regulatory authorities.

# Agents Affecting Quality in Stored Grains

There is a large range of quality changes that may occur during the storage of grains. These changes may be brought about by physical, biological, or chemical agents.

The primary aim of most gaseous treatments of stored grain is to control the biological agents causing quality change within the stored commodity or its containing structure. These agents are normally animal pests, usually insects, but may include rodents. The biological agents themselves can cause substantial physical damage to the grain quality by completely or partially consuming it, or through contamination. Killing the biological agents will eliminate direct damage and may also lead to a reduced risk of consequential quality degradation by other biological, chemical and physical factors.

Controlled atmospheres with substantially reduced oxygen concentration have the potential to kill animals (insects, mites and rodents), reduce other biological activity (moulds, fungi, and grain respiration), and to reduce oxidative degradation. However, CAs with high carbon dioxide concentrations in air, and which have a significant oxygen content, act as a toxic gas only. While able to kill pest animals they are unlikely to have any other direct quality preserving effects (Banks 1981). Because the component gases of controlled atmospheres are normal components of the storage atmosphere, it is unlikely that they will directly cause quality degradation by residue formation. There is, however, some evidence that, although high CO2 atmospheres generally have no adverse effect on germination, there are specific circumstances when germination may be affected (Peterson et al. 1956; Ponton and Briggs 1969; Banks and Gras 1982).

Fumigation on its own is unlikely to have any direct positive effect on grain quality other than control of biological degradation. Fumigants may have negative effects on grain quality by reducing germination or by forming detectable and/or deleterious residues (Plimmer 1977).

# Similarities between CAs and Fumigants

Fumigants and controlled atmospheres are gaseous treatments and have much in common in both the theory and practice of their application. They require similar facilities, can have a similar role in an integrated commodity management system (Annis and Graver 1987) and their use has indirect but important consequences leading to quality maintenance.

If a storage enclosure is well sealed and adequately dosed with an insecticidal atmosphere, the gas has the potential to come in contact with every grain in the storage, thereby giving a high probability of complete disinfestation. If the grain is dry enough to store safely, and is protected from further infestation and the effects of physical agencies such as excessive moisture, it may be stored for extremely long periods with little risk of significant quality degradation. Gaseous treatment, therefore, if properly carried out in an adequately sealed and gas-proof enclosure, not only gives reliable disinfestation but allows a high degree of continued physical protection from external biological and physical agents that may otherwise degrade the stored commodity.

The use of a semi-permanent enclosure for physical protection has been advocated before (e.g. McFarlane 1980). However, without thorough disinfestation and a reliable means of protection against reinfestation it may lead to significant quality degradation. Live insects can cause substantial localised heating and water production. This heat will lead to moisture migration that cannot escape from an unventilated system, leading in turn to the formation of wet areas of grain close to the inside of the fabric of the enclosure, if this is in contact with the grain. If the grain is not in contact with the fabric, water from the high humidity air may condense on the inside of the enclosure and otherwise come into contact with the grain. In both cases there is a significant likelihood of mould growth, sprouting, etc. These biological processes themselves produce further heat and water, thus exacerbating the problem.

However, a sealed enclosure that does not lead to significant moisture migration can be left safely in place. The enclosure then forms a barrier, which if properly maintained should stop reinfestation by insects, help protect the commodity from rodents, dirt and dust (Tilton 1961), reduce the impact of ambient humidity (Annis and Greve 1984) and aridity, and offer some protection against water ingress, be it from roof leaks or low level flooding.

### Criteria for a Gaseous Treatment

The first objective of a gaseous treatment should be to kill all target organisms. This is equally true whether the treatment is for quarantine or is a component of long-term storage. A complete kill can be assured only by maintaining an adequate concentration of active gas for long enough and throughout the storage to achieve the required effect (in the case of oxygen-deficient atmospheres, a sufficiently low oxygen concentration is the objective). In insect control, this means 100% mortality in all stages of all species present. It is often difficult to be certain which insect species are present. The dosage, in terms of time and concentration, has therefore to be set so as to ensure a complete kill of the most tolerant insects likely to be present.

Most existing grain storage facilities were designed to be well ventilated. Gaseous treatments require a sealed enclosure. Thus, there are very few existing storage facilities in which very reliable gaseous treatments can be carried out without some modification to either the storage and/or existing fumigation practices. The modifications necessary are in three main areas: sealing, dosing and distribution. The general specification of these modifications is given later and the details for particular treatments are given elsewhere (AFHB/ACIAR 1989). If these specifications cannot be met, a gaseous method of quality control should not be considered. If, for some reason, a gaseous treatment has to be carried out in suboptimal conditions, the risks associated with the treatment failing need careful consideration and a plan made to cope with the consequences of the almost certain failure.

#### What is a Failure?

There are a number of criteria for a treatment failure (Banks and Annis (1984a) discuss criteria for a successful fumigation). In commercial practice, the least stringent of these is finding significant numbers of insects after the fumigation. The most stringent, rarely considered in commercial fumigation, is identification of localised areas in the grain where dosages would have been inadequate for a complete kill had insects been present. In this paper, a practical definition of failure is used: that there is survival by the target organisms at such a level that there is a possibility of population resurgence from these survivors.

#### **Risks Associated with Failure**

The immediate impact of insect resurgence depends on the reason for treatment. In traditional treatments, a failure is often considered merely as a nuisance that requires retreatment. In long-term sealed storage a failure may compromise the quality of the enclosed commodity. In quarantine treatments, failure may lead to the loss of whole markets. A less immediate but more serious long-term risk is that survival may lead to insects developing tolerance/resistance to the treatment, thus making the requirements for successful treatments in the future harder or, in the worst case, impossible to meet. The problems created by resistance are many but some of them are: the cost of using higher doses; increased exposure times requiring continuous or repeated fumigant application; and production of unacceptable levels of residue with some fumigants.

# The Prerequisites for Quality **Control Using Gases**

In the simplest of terms, the most important requirement for a successful gaseous treatment is to maintain at least a minimum gas concentration for a required period throughout the enclosure. Guidelines for these requirements are shown in Table 1. The idea of requiring a minimum concentration at the end of exposure is not a well-recognised concept in fumigation. It is used in this paper to eliminate problems associated with assuming that the  $c \times t$  products for a given response are constant for gases such as carbon dioxide, phosphine and low oxygen.

The minimum concentration goals are set at levels appropriate to current good fumigation practice, but other combinations of concentration and time can be equally effective (see Winks (1987) for phosphine and Annis (1987) for low oxygen and carbon dioxide).

None of these targets can be achieved or maintained if:

- · inadequate gas is added;
- · there is excessive leakage leading to dilution by air;
- poor gas distribution occurs; or
- · other processes occur that delay the establishment of an even concentration.

Theoretically, any of these can be accommodated by adjusting one or more of the three factors controlling gas concentration, namely level of sealing, method of gas distribution, and gas application methodology. Examples of the relationship between sealing and concentration distribution are discussed by Banks and Annis (1984a). They showed that with a single-shot addition of fumigant (phosphine in the case in point) it was essential that the gas be retained well enough to ensure adequate concentration distribution before losses reduced the average concentration to non-efficacious levels.

The interaction between application methodology and sealing is complex and not well documented, although it is considered by Annis elsewhere in these proceedings (Annis 1990). Generally, in a single-shot fumigation, it is not possible to increase applied dosage enough to overcome the effect of very high leakage rates. For example, a loss rate of 50% per day means a reduction to 1/33 of the original concentration during a fumigation of 7 days (the time of a phosphine fumigation) and a reduction to 1/1808 in 15 days (the time of a carbon dioxide treatment). In both cases, the required initial concentration would need to be impossibly high to meet the target.

Loss rates of 50% or higher are common in unsealed storages. Unacceptably large initial dosages may be required, even when some attempt, albeit inadequate, has been made to achieve gas-tightness. For example, the method of fumigation of bagstacks using gas-proof sheeting and sand-snakes may well not give adequate sealing to reduce the CO, loss rate to the 7.0% per day required for a single-shot treatment where the upper concentration possible is 100% and a minimum of 15 days above 35% is needed. On the other-hand, in a wellsealed storage it may be possible to ensure that

| Gas              | Days <sup>a</sup> | Concentration        | Ct product             | Reference       |
|------------------|-------------------|----------------------|------------------------|-----------------|
| carbon dioxide   | 15 days           | > 35%                |                        | Annis 1987      |
| low oxygen       | 20 days           | < 1%                 | _                      | Annis 1987      |
| phosphine        | 7 days            | $100 \text{ mg/m}^3$ |                        | b               |
| methyl bromide   | 1-2 days          | -                    | 150 g h/m <sup>3</sup> | AFHB/ACIAR 1989 |
| hydrogen cyanide | 1 day             | C                    |                        |                 |

Table 1. Suggested dosage targets for gaseous treatments of grain at 25°C

<sup>a</sup> In cases of slow gas introduction or poor gas distribution it is necessary to increase the exposure period to ensure the required time above the minimum concentration is achieved throughout the enclosure. <sup>b</sup> Based on the dosage to ensure high mortality in *Sitophilus granarius* pupae (Winks 1987).

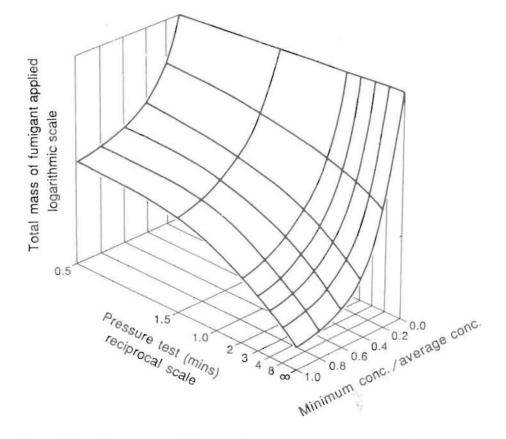
<sup>c</sup> Concentration that needs maintaining not defined.

target dosage regimes are reached even if the dose is decreased substantially from those normally recommended. The actual minimum applied dose required in these circumstances is correlated with the level of sealing as assessed by a pressure test (Banks 1987; Annis 1990).

It is possible to approximate the combination of distribution, applied dose, and level of sealing required to meet the dosage schedules given in Table 1. This can be done by applying the method of Banks and Annis (1984b) to both one-shot and continuous-application fumigations to give the treatment surfaces of the type shown in Figure 1. Combinations of dose and pressure, and distribution above the surface, will meet the requirements of Table 1, those below will fail.

Toxicological constraints may make the restrictions on increasing the initial concentration even more severe. The response of insects to high concentrations of some fumigants may be significantly different in terms of concentration and time requirements than would be predicted from the response at lower concentrations. This may make treatments at high concentration less desirable than at lower ones and, in some cases, may necessitate prolonging the treatment rather than reducing it for high concentrations. Fumigants reported to display different effects at high and low concentration include phosphine (Winks 1984) and carbon dioxide (Annis 1987).

One further limitation to simply increasing concentration by adding more gas initially is that it does nothing to overcome the effects of unidirectional leakage. This type of leakage is caused by two major phenomena, a difference in the density of internal and external gases (chimney effect) (Banks and Annis 1984b) and by differential wind-induced pressure between the base and top of (or across) the enclosure (Mulhearn et al. 1976). Both phenomena can cause substantial and continuous ingress of air thereby reducing the gas concentration in localised areas. This type of unevenness in concentration can be reliably countered only by either one of two methods. Either the leaks are identi-



**Fig 1.** An example of a surface plot showing the combinations of pressure test, total dose, and distribution needed to ensure that a fumigation meets a defined minimum concentration at a specified time. Combinations falling below the surface will fail, those above will pass. This example is based on the data for a horizontal grain shed in Banks and Annis (1984b).

fied and sealed, or all areas inside the enclosure must be held at a constantly positive differential pressure compared with the external environment. If the second method is employed then gas loss during pressurisation must be replaced.

On the other hand, uneven distribution of concentration resulting from poor initial distribution of gas may be overcome by one or other of the following four ways:

- 1. better initial gas distribution by ducting, etc.
- 2. gas distribution assisted by ducts and fans
- additional sealing to allow uniform distribution before loss
- continuous/repeated addition of gas to make up for losses.

There is no single prescription for meeting concentration/time requirements. In theory at least, they can always be met by one or many combinations of sealing, distribution method and dosage (method and quantity). The balance between these will depend on a variety of operational factors, with those most commonly taken into consideration being cost and convenience. In some circumstances it may well be that, although a theoretical prescription can be produced, no economically acceptable solution can be derived. In this case, an alternative to a gaseous treatment will have to be considered.

The following examples taken from reports of well-monitored gaseous treatments show that it has been possible to achieve target schedules in a wide range of storage enclosures. Although all are based on Australian work, similar work has been reported from elsewhere, e.g. China (Lu Quianyu 1984) and USA (Jay et al. 1990).

#### Case 1

Type of structure: well-sealed bag-stack.

Load: 100-200 t rice, paddy, and maize.

- *Enclosure material:* a PVC membrane tailored to stack dimensions, sealed to PVC floor sheet (indoor storage).
- Level of sealing: pressure halving time 100–50 Pa > 10 min (typically > 20 min).
- Treatment method: single addition of carbon dioxide or phosphine generating preparation.
- *Distribution:* **a.** With carbon dioxide, initial purge plus time for natural convection to ensure all parts were above 35% for 15 days before leakage made this unattainable.

- b. With phosphine, natural convection and diffusion to ensure all parts were above 100 mg/ m<sup>3</sup> for 7 days before leakage made this unattainable.
- *Proven protection:* with  $CO_2$  up to 18 months with milled rice, up to 1 year with paddy and maize. With phosphine up to 6 months for milled rice and maize.
- References: Annis and Graver 1986; Sukprakarn et al. 1990; Sabio et al. 1990; Anon. 1984; Annis 1990.

#### Case 2

Type of structure: bunker storage bulk grain.

- Load: 10 000 t Australian standard white (ASW) wheat.
- Enclosure material: PVC membrane top-cover, bitumenised paper floor cover.
- Level of sealing: pressure halving time 100-50 Pa approx. 3 min.
- *Treatment method:* single addition of phosphine generating preparation at a rate of 0.75 g PH<sub>3</sub>/t.
- *Distribution:* natural convection and diffusion ensure all parts are above  $c \times t$  product > 20 g h/m<sup>3</sup> in 28 days.

Proven protection: 10 months.

Reference: Banks and Sticka 1981.

#### Case 3

- Type of structure: very large shed bulk grain storage.
- Load: a. 176 000 t wheat; b. 278 000 t wheat.
- Enclosure material: concrete walls and floor, aluminium cladding, sealed after construction (Ripp 1984).
- *Level of sealing:* **a.** Pressure halving time 170–85 Pa 28 min. **b.** Pressure halving time 200–100 Pa > 30 min.
- *Treatment method:* **a.** Single addition of phosphine generating preparation at a rate of 0.88 g PH<sub>3</sub>/t. **b.** Initial purge followed by daily addition of carbon dioxide to keep concentration above 35%.
- *Distribution:* fan-assisted recirculation between base and head space such that **a.** all parts above 100 mg/m<sup>3</sup> phosphine for 7 days; **b.** all parts above 35% CO<sub>2</sub> for 23 days.

Proven protection: not stated

Reference: Green 1987.

#### Case 4

Type of structure: large shed — bulk grain storage.

Load: a. 16 000 t wheat; b. 16 000 t wheat.

Enclosure material: steel cladding walls and roof, sealed after construction.

*Level of sealing:* pressure halving time 100–50 Pa 5 min.

Treatment method: **a.** Initial purge with 100%  $CO_2$ . **b.** Single addition of phosphine preparation at a rate of 1.6 g PH<sub>3</sub>/t.

*Distribution:* **a.** Fan-assisted recirculation between base and head space such that all parts above 35% CO<sub>2</sub> for 15 days. **b.** Natural convection and diffusion so that all parts above 100 mg/m<sup>3</sup> PH<sub>3</sub> for 7 days.

Proven protection: a. 3-4 months; b. >4 months

References: Sealing: Banks et al. 1979; CO<sub>2</sub> results: Banks et al. 1980; PH<sub>3</sub> results: Banks and Annis 1984a.

### Case 5

Type of structure: ISO general purpose shipping container (6.1 m).

Load: various dry commodities about 18 t.

- Enclosure material: steel walls and roof, plywood floor.
- Level of sealing: pressure test decay time of >10 sec.

Treatment method: initial charge of dry ice for purging. Continuous addition of gas by controlled sublimation of dry ice.

Distribution: natural convection.

Proven protection: duration of domestic transit and voyage to Europe, 1-2 months.

Reference: Banks 1987.

#### Case 6

Type of structure sealed steel vertical cells. Load: 1900 t ASW wheat.

Enclosure material: welded steel.

- Level of sealing: pressure halving 1500-750 Pa 3.6 min.
- Treatment method: single addition carbon dioxide.

Distribution: recirculation base to head-space.

Proven protection: 4.5 months.

Reference: Wilson et al. 1980.

#### Case 7

Type of structure: sealed steel vertical cells.

Load: 1900 t wheat.

Enclosure material: welded steel.

*Level of sealing:* pressure halving > 5 min.

Treatment method: continuous addition nitrogen.

Distribution: aeration ducts at base.

Proven protection: not stated.

Reference: Banks et al. 1980.

In all these cases, sealing and proving the level of sealing were major aspects of ensuring the maintenance of target gas concentrations. All rely to some extent on adequate initial dosing, but in case 3b (very large shed with  $CO_2$ ), case 5 (ISO shipping container with  $CO_2$ ) and case 7 (vertical silo with nitrogen), some form of concentration maintenance was also necessary.

In the very large shed, the large volumes of purge gas needed to attain the initial high concentration required for a single-shot treatment were logistically very difficult to apply. In this case, however, addition of  $CO_2$  when required for maintenance at >35% presented no difficulties.

Treatments of shipping containers with  $CO_2$  presents a problem because it is almost impossible to select a container that can be sealed well enough for a conventional single-shot treatment. It is therefore necessary to select containers to a lower level of gas-tightness and, over several days after the initial gassing, add make-up  $CO_2$  produced by the controlled sublimation of dry ice.

In treatments relying on low oxygen it is not feasible, because of pressure build up, to seal sufficiently to use a single-shot treatment of gas to maintain <1.2%  $O_2$  for 21 days or more. This means that in low oxygen treatments, continuous or on demand addition of low-oxygen gas is needed to displace the oxygen gained by leakage.

Recent advances in atmosphere generation technology may well alter the balance of effort between sealing, addition, and distribution in such a way as to remove some of the emphasis from sealing towards constant introduction of gas. Although these changes have been foreshadowed, e.g. phosphine addition (Winks 1990) and low cost, burner-generated, low oxygen atmospheres (Banks 1984), they have not yet been reported as being either widely or readily available.

Until these processes become widely and economically available, sealing remains the most reliable, currently available method of ensuring efficacious gaseous treatments. Because of this a good starting point for any gaseous treatment is to aim for an enclosure sealed to the highest standard that is economically and logistically possible. Sealing is neither as hard nor as complex as it appears, although it does require some experience. Given the correct experience, common sense and a reasonable range of sealing materials there a very few enclosed structures that can not be well sealed (Ripp 1980).

### Conclusion

The foregoing discussion implies that many gaseous treatments (as currently carried out) are not up to the required standard. The three or four gases we have available today as major agents for quality control are all we are likely to have for a long time. Methyl bromide, phosphine, carbon dioxide and, possibly for some applications, hydrogen cyanide, all live a precarious life. Each has its weaknesses in terms of potential for resistance, perceived danger to the environment, expense, residues, and operational difficulties. More care is therefore needed to ensure their availability as fumigants is preserved for as long as possible. This implies that they have to be used in a manner safe to the environment, workers, and consumers, as well as being 100% effectively against insect pests. In practical terms that means minimum emission to the environment, the lowest possible residue in the commodity and well-planned and executed treatments in suitable facilities. The simplest way of achieving this at present is to make the fumigation enclosure as gas-proof as possible.

In a limited number of applications it will not be possible to achieve targeted concentration regimes solely by a combination of sealing and single dosage. In these cases, a method of external concentration maintenance will be needed. Even then, however, a substantial level of sealing will be required to ensure reliable treatments. Where the targeted concentration regimes cannot be achieved, fumigation and controlled atmospheres are not options for quality control and other methods must be employed.

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