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# APPLICATION OF FUMIGANTS AND MODIFIED ATMOSPHERES FOR SAFE STORAGE OF FOOD GRAINS

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Acharya N. G. Ranga Agricultural University Agricurtural College, Bapatla India being an agrarian country signifies the importance of Agriculture and hence the backbone of the country's national economy.

Approximately 67% of the working population in this country belongs to the Agriculture sector.

Also India being the 2<sup>nd</sup> largest populated country demands a high amount of food grain consumption in the country and the per-capita availability of food grains has been recorded as 492g/day.



### Estimated post-harvest losses in India

### **History of Fumigation**

Fumigation has been used since ancient times to <u>'purify the air</u>', perhaps due to the observation that smoke chased away insects, which were always suspected of causing <u>human and animal</u> <u>disease.</u>

In the year 429 BC, fumigation was recommended by Hippocrates for controlling an epidemic which affected animals and humans in Athens. The method consisted of burning <u>odoriferous herbs</u> in streets of the city, and was credited with halting the epidemic.

Fumigants were used (431-404 B.C.) as a weapon when the saturated wood and sulphur and burned the walls of a fortified enemy. They also used poisonous gases during World War I.

In the 5th century AD <u>Hierocles</u> against bacterial disease by the Persians for use against cattle plague . During an outbreak of <u>cattle plague at Montpellier</u> in 1745, he recommended <u>fumigation of cowsheds with wood and vinegar</u>.

<u>Chabert</u>, in 1774, also recommended using fumigation in the control of <u>anthrax</u>.
In 1805, <u>Huzard</u> recommended an alternative recipe for use against the anthrax disease, which consisted of burning a mixture of gunpowder, common salt, and crushed juniper berries and wood (17).

- Fumigation, as a method of insect control, has been known for many centuries, the fumes of sulfur having been used as early as the 12th century.
- These poisonous gases has helped development many of the modern fumigants and techniques employed in commercial fumigation today.



**Sulfur fumes** 



Mexican laborers being fumigated with the pesticide DDT in Hidalgo, Texas, in 1956 7

#### **Fumigation method**



#### Injury due to mustard gas Fumigation



Traditional SULFUR Fumigation of rolled cinnamon (closed chamber process continues till all the cinnamon is yellow in color – open air restores original color in about 3 months)



Liquid fumigant

protection

### **FUMIGATION**

Fumigation is a method of pest control that completely fills an area with gaseous pesticides or fumigants to suffocate or poison the pests within.



Fumigants are gases that penetrate the grain mass to kill insects. These are widely used for pest elimination in all stored products that include cereals, oilseeds, pulses, spices, dried fruits and their processed foods, to prevent economic and quality losses due to insect pest attack.

### **Desirable attributes of a Fumigant**

**Toxicity over short exposure periods** 

High diffusion and penetration potential

Insignificant or tolerable amounts of residues

Decompose into compounds harmless to the environment.

Easy to handle

#### **Easy to detect and monitor**



## **Types of Fumigants**



Fumigants	Trade Names	Used against stored pests
Aluminium Phosphide	Fumitoxin Phostoxin Phostek, Celphos	Wheat, Barley, Rye, cereals, Millets, Rodents
Chloropicrin	Chlor-O-Pic	Cleaning empty grain bins
Methyl Bromide	Meth-O-Gas Brom-O-Gas	Soil fumigant, Wheat, corn, sorghum
Sulfuryl fluoride	Vikane, Profume, Xunmiejin	Wood, flour mills, food factories, dried fruits, cereal grains, termites.
Carbonyl sulfide	Cosmic. Boc	Post harvest pests in all stages including Mites.

Fumigants	Trade Names	Used against stored pests
Hydrogen Cyanide		Food stuff, Grain and Seed
Ethyl Formate	Vapormate	Cereal grains, soil fumigant against Nematodes
Carbon Disulfide		Bulk grains storage
Methyl Iodide		Soil inhabitant pests and Termites
Ozone		Kills stored product and also inhibits mold spore development.
Volatile essential oils of Botanical origin	Alkoloides	Stored product insects

# Sealing

- Sealing is the hardest and most important part of any fumigation.
- It sterilizes the grain, killing insects in all stages and other vermin that may be present.
- It prevents absolutely, the entry of insects and rodents .
- It prevents grain moisture content from becoming mouldy.



### **Methyl bromide**

Methyl bromide is a colorless, odorless, tasteless, gaseous fumigant marketed as compressed, liquefied gas.

Methyl bromide is nonflammable, penetrates grain well and provides a very rapid kill of insect pests.

The established threshold limit of methyl bromide exposure is 15 ppm

Repeated exposure to high dosages allows methyl bromide to accumulate in body tissues and may eventually cause chronic symptoms including blurred vision, dizziness and staggering, and mental imbalance.





#### **Montreal Protocal – Methyl Bromide**

- Methyl bromide was recognised as an ozone-depleting substance under the Montreal Protocol and control measures for the chemical was included in the Amendment in 1992 under Article 2H of the Protocol.
- Methyl bromide used only for quarantine and pre-shipment.





### Phosphine (PH<sub>3</sub>)

- Phosphine or hydrogen phosphide (PH<sub>3</sub>) 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.

 $AIP + 3H_2O \longrightarrow PH_3 + Al(OH)_3$  $Mg_3P_2 + 6H_2O = 2PH_3^{+} + 3Mg(OH)_2$ 

### Phosphine should not be used

Where resistance is known to exist

At low temperatures below 15<sup>o</sup> C

Where a rapid treatment is required (< 7 days).

In areas adjacent to workplaces and habitations.

Where there is no trained and qualified team.





# Aluminium phosphide pellets

#### **Phosphine resistance**

- The continuous and discriminate use has resulted in evolution of resistant populations to phosphine.
- Resistance to phosphine have been developed in the stored grain pests such as *Sitophylus oryzae, Rhyzopertha dominica, Tribolium castaneum* and *Oryzaephilus surinamensis.*

#### Lethal doses (mg/L) of phosphine against the most susceptible and the resistant strains of field collected grain insect pests.

Insect (Susceptable)	LD <sub>50</sub> (fiducial limits)	LD <sub>95</sub> (fiducial limits)	
Sitophylus oryzae	0.004	0 .010	
Rhyzopertha dominica	0.006	0.074	
Tribolium castaneum	0.138	1.054	
	Resistant		
Sitophylus oryzae	1.70	6.11	
Rhyzopertha dominica	3.61	6.84	
Tribolium castaneum	1.33	3.41	

#### **Detecting devices for fumigation**

#### Gas detector tube pump





*If you are not monitoring, You are not fumigating...* 





### **Factors effecting Fumigation**

### Sorption

- Temperature
- Grain Moisture
- Grain type and condition
- Insects
- Storage facility
- Dosage and time of exposure

#### Minimum exposure periods for controlling insects (2 AIP tablets/m<sup>3</sup>)

		Exposure period	
Stored grain pests	Scientific Name	≥ 20 <sup>0</sup> C	10 – 20 <sup>0</sup> C
Rice weevil	Sitophilus oryzae	12 days	16 days
Khapra beetle	Trogoderma granarium	10 days	16 days
Groundnut bruchid	Caryedon serratus	10 days	14 days
Paddy moth	Sitotraga cereallela	7 days	10 days
Rice moth	Corcyra cephalonica	7 days	10 days
Tropical ware house moth	Ephestia cautella	7 days	10 days
Pulse beetle	Callosobruchus spp	7 days	10 days
Flat grain beetle	Cryptolestes spp	7 days	10 days
Coffee bean weevil	Araecerus fasciculatus	7 days	10 days
Spice beetle	Stegobium paniceum	7 days	10 days
Psocids	Liposcelis spp	10 days	14 days
Lesser grain borer	Ryzopertha domanica	7 days	10 days

### **Application methods of Fumigants**



- Direct mixing (vertical storage)
- Surface application storage)
- Large Bulk Fumigation
- Farm storage fumigation
  - "Hot spot" fumigation
- Recirculation
- Forced distribution
- Stack Fumigation







#### **Direct mixing (vertical storage)**

The fumigant is applied to the grain so that it is distributed as evenly as possible from the beginning of the treatment.

Direct mixing is often employed when infestation is general throughout the mass and when there is access to the grain stream during filling or transfer from one bin to another.

Only solid or liquid-type fumigants are used in this method.

**Eg: Aluminium Phosphide** 



### Surface application (flat storage)

The liquids are sprayed evenly over the top surface of the grain and the vapours slowly evolve and diffuse downward through the bulk.

This methods of application of fumigants to the surface of stored grain is influenced by the size and type of storage.

Ex: Carbon disulphide, Propylene oxide



#### **Large Bulk Fumigation**

The solid and liquid-type fumigants are usually applied to the surface of bulk grain by means of sprayers. If the surface area is large, power sprayers may be used.

To facilitate the rapid application of the liquid to the surface of the grain for bulks up to 30 000 bushels, a sprayer which delivers the liquid at the rate of 35 to 55 1 gallons per minute.

For larger bulks, adequate hose and a pump capable of throwing a stream about 25 m at the rate of 100 gall per minute should be used.

#### Ex: Methyl bromide, Phosphine





## Farm storage fumigation



The gas tightness of the structure is particularly important in small storages, because the mass of grain is not large enough .

Steel, concrete or tight wooden structures are used.

If Aluminium phosphide is used, it is recommended that a tarpaulin or polyethylene sheet be placed carefully over the surface of the grain after the tablets are applied.

### Hot spot fumigation

"Spots" are usually recognized and defined by a local rise in temperature. The respiratory activity of the insects leads to an increase in the temperature and the humidity. "Hot spots" are formed. If the temperature in one of these "hot spots" passes 40°C, it becomes too hot for the insects and they will move to cooler surroundings. The "hot spot" thus spreads.

Enough fumigant should be applied to maintain the required lethal concentration, not only in the region of infestation, hut also in the margins surrounding it for 1 or 2 m in every direction to the spot itself.

The vapours from the marginal treatments tend to slow down diffusion of the fumigant from the infested spot.

#### **Ex: Aluminium phosphide tablets**



### Recirculation

For the treatment of bulk grain, recirculation of the fumigant by means of permanent or temporary installations provides an effective and economical means of insect control.

Recirculation is only applicable when the walls of the storage units are sufficiently gas tight to prevent the fumigant/air mixture from being forced out while under positive pressure exerted by the fan.

Ex: Methyl bromide, Hydrogen cyanide



### **Stack Fumigation**



- This method consists of two PVC sheets; one to cover the floor and the other to cover the stack; both are bonded chemically to a sealed enclosure.
- This method of fumigation of stacks has proven satisfactorily for the application of phosphine or carbon dioxide.



### Disadvantages

- Unacceptable pesticide residues especially imposed by some importing countries that are not recognizing codex MRL's.
- High development costs and time required for chemical manufacturers to register grain protectants for commercial use.
- The requirement for achieving nil tolerance for live insects in export grain commodities (including raw cereals and milled products).
- Environmental and social implications.

# Case study 1 : Ozone to control *Rhyzopertha dominica* (Coleoptera: Bostrichidae) in stored wheat grains. (Nelson *et al.*, 2016)

Study area	Brazil
Fumigant	Ozone
Replications	3
Statistical tool	Analysis of variance and Regression
Pest	Rhyzopertha dominica



Source: Journal of Stored Products and Postharvest Research . 7(4) : 37-44 Mean values of the instantaneous growth rate of *Rhyzopertha dominica, distributed over the plenum and in the middle and superficial layers of the wheat grain column exposed to ozone gas and atmospheric air (control) at a concentration of 1.61 mg/L at different lethal times (LT) after 60 days of storage.* 

	LT (h)	Instantaneous growth rate			
Ireatment		Basis	Middle	Surface	
	LT <sub>10</sub>	0.018	0.017	0.020	
Ozone	LT <sub>30</sub>	0.013	0.012	0.012	
020116	LT <sub>50</sub>	0.003	0.004	0.004	
	LT <sub>70</sub>	0.001	0.003	0.002	
	LT <sub>90</sub>	0.000	0.000	0.000	
	LT <sub>10</sub>	0.021	0.022	0.021	
Control	LT <sub>30</sub>	0.021	0.022	0.020	
	LT <sub>50</sub>	0.022	0.020	0.020	
	LT <sub>70</sub>	0.022	0.021	0.021	
	LT <sub>90</sub>	0.021	0.021	0.020	
				34	



Figure 1. Instantaneous growth rate of *Rhyzopertha dominica* exposed to ozone gas and air (control) treatments, according to the lethal time, at a concentration of 1.61 mg L<sup>-1</sup> after 60 days of storage.

The r<sub>i</sub> of *R. dominica* decreased as the exposure time of the wheat grain ozone gas increased.
 In contrast, the atmospheric air

(control) did not affect r<sub>i</sub> of *R. dominica* in any of the exposure periods. Case study 2 : Efficacy and Limitations of Phosphine "Spot-Fumigation" against Five Coleoptera Species of Store Product Pests in Wheat in a Grain Store.

#### (Aulicky and Stejskal, 2015)

Application method	Spot- Fumigation	
Crop seed	Wheat	-2/12
Data evaluation	Bio-assay	

#### Source : Journal of Plant Protection Sciences, 51: 33-38



Figure 1. Layout of the flat grain store with sampling locations. One sample (circle) position contained 5 containers with pests located at 0.1 m depth of grain and 5 containers at 1 m depth of grain Black circle – position of sample located inside fumigated spot. White circle – position of sample outside fumigated spot Grey zone – fumigated spot of grain mass (560 t) under sheet. Table 1. Efficacy of PH3 (average percentage mortality + SE) at various distances (0–15 m) from the PH<sub>3</sub> fumigation spot on 5 species of pests located 1 m below the grain surface

Located 1 m below	0 m	5 m	10 m	15 m	Control
Sitophilus granarius	100.00 ± 0.00	11.67 ± 3.33	3.33 ± 3.33	1.67 ± 1.67	0.00 ± 0.00
Rhizopertha dominica	100.00 ± 0.00	1.67 ± 1.67	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
Tribolium castaneum	100.00 ± 0.00	5.00 ± 2.89	1.67 ± 1.67	1.67 ± 1.67	0.00 ± 0.00
Oryzaephilus surinamensis	100.00 ± 0.00	50.00 ± 8.66	38.33 ± 10.14	10.00 ± 2.89	6.67 ± 1.67
Cryptolestes ferrugineus	100.00 ± 0.00	23.33 ± 13.02	10.00 ± 2.89	3.33 ± 3.33	0.00 ± 0.00





# Table 1. Efficacy of PH3 (average percentage mortality + SE) at various distances (0–15 m) from the PH3 fumigation spot on 5 species of pests located 0.1 m near the grain surface

Located near 0.1 m	0 m	5 m	10 m	15 m	Control
Sitophilus. granarius	100.00 ± 0.00	10.00 ± 5.77	6.67 ± 3.33	1.67 ± 1.67	1.67 ± 1.67
Rhizopertha. dominica	100.00 ± 0.00	3.33 ± 1.67	1.67 ± 1.67	0.00 ± 0.00	1.67 ± 1.67
Tribolium castaneum	100.00 ± 0.00	1.67 ± 1.67	1.67 ± 1.67	1.67 ± 1.67	0.00 ± 0.00
Oryzaephilus surinamensis	100.00 ± 0.00	41.67 ± 19.65	28.33 ± 6.67	23.33 ± 11.67	6.67 ± 3.33
Cryptolestes ferrugineus	100.00 ± 0.00	33.33 ± 25.87	3.33 ± 3.33	3.33 ± 1.67	0.00 ± 0.00





Decline of PH3 efficacy (expressed as % pest mortality) with the increasing distance (5, 10, and 15 m) outside the fumigated spot.

#### **Modified Atmospheres**

Modified atmosphere is the composition of atmospheric gases or their partial pressures in the treatment enclosure have been modified to create a favourable for the control of storage insects.



#### **Requirements for application of Modified atmospheres**

• Based on atmospheric composition and its biological effect two main types of modified atmospheres are present.

Low oxygen atmosphere have been to be insecticidal below 2% oxygen to all species and stages of stored product pests. Some species are more susceptible and may killed at 3%.







High carbon dioxide atmosphere must contain a substantial proportion of more than 60% kills stored product insects. At 26° C about four days of exposure would be sufficient to kill all stages of insects.

### Hermetic storage

Hermetic storage of grain was practiced in ancient times in underground pits in the dry, subtropical regions of the Middle East and other dry regions of the world, such as Africa and India.

It also termed sealed storage or airtight storage or sacrificial sealed storage.



This method takes advantage of sufficiently sealed structures that enable insects and other aerobic organisms in the commodity or the commodity itself to generate the MA by reducing oxygen ( $O_2$ ) and increasing carbon dioxide ( $CO_2$ ) concentrations through respiratory metabolism.

#### **Applications of Modified atmospheres**



#### Effects of modified atmospheres on product quality

Generally, the lower the moisture content and the lower the temperature, the longer the seed can be stored . (Copeland and McDonald, 1985)

Seeds below their critical moisture content are not significantly affected by high-CO<sub>2</sub> or low-O<sub>2</sub> atmospheres.

With increasing grain-moisture contents, carbon-dioxiderich atmospheres could reduce the physiological quality of grain by interfering with the enzymatic activity.

If preservation of germination is of primary importance, the use of  $CO_2$ -free and low- $O_2$  atmospheres is preferable. Case study 3 : Management of Pulse Beetle, *Callosobruchus maculatus*(F) Population by Nitrogen Based Modified Atmosphere. (Ingabire *et al.*, 2013)

Study area	Post-Harvest Technology Centre, (PHTC) Tamil Nadu Agricultural University (TNAU) campus, Coimbatore	
crop used	Green gram seeds (variety CO6)	
Stored pest	Callosobruchus maculatus	
Modified atmosphere	Nitrogen	
Statistical tool	ANOVA by SAS	

Source: Journal of Entomology and Zoology Studies. 2013; 1 (5): 48-52

#### Effect of nitrogen based modified atmosphere on adult mortality of *C. maculatus*

0 <sub>2</sub>	Per cent adult mortality after different exposure periods			
concentration	3 days	5 days	7 days	Mean
N1 - 14% O <sub>2</sub>	41.5	44.8	66.7	51.0
N2 - 11% O <sub>2</sub>	51.3	62.4	76.8	63.5
N3 - 8% O <sub>2</sub>	63.2	75.1	81.7	73.3
N4 - 5% O <sub>2</sub>	73.0	85.1	92.2	83.5
N5 - 2% O <sub>2</sub>	82.9	92.8	100.0	91.9
N6 - Control	4.4	8.9	13.3	8.9
Mean	52.7	61.5	71.8	

The mortality of pulse beetle by counts made at 3, 5 and 7 days of exposure. The adult mortality was found to be high (91.9%) at 2% O2 when compared to other concentrations. At 14%, 11%, 8% and 5% O2 concentration, the mean per cent adult mortality recorded was 51.0, 63.5, 73.3 and 83.5 respectively. In addition, the exposure period influenced significantly the adult mortality of *C. maculatus*.

#### Case study 4 : The Effect of Low Pressures on the Mortality of Six Stored-product Insect Species (Calderson *et al*, 1966)



FIG. 1. Equipment used in studying the effects of reduced pressure on insects.

Initially, the pump was operated with taps A, B, C, open, and tap D closed.
The pump was operated with taps D and A closed and B and C open.
When the manometer gave a reading of 10 mm tap C was closed and A opened.
The resulting reading gave the pressure in the container.

Source: Journal of stored product research, 2: 135-140.









The susceptibility of the test insects to low pressure is affected by temperature: at the higher temperature used (25°C) insect mortality was higher than at the

lower temperature (18° C)

### Conclusions

- Modified Atmospheres and Fumigation are the only two applications used for bulk mass of grains, to protect against the storage pests.
- Both of them can be an alternate methods for insecticides sprays.
- Handling, Precautions taken during the applications, correct dosages makes the effective usage of fumigants.

