

*7th International Workshop  
How to handle imported containers safely  
Berlin, May 22 - 23, 2014*

## Regulations of and authorization for application of fumigants

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### The purpose of fumigation

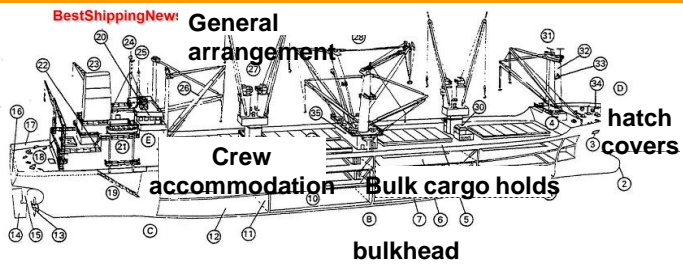
**In the trans-continental shipping of goods:**

- “ Protection of **goods** from spoilage by animals and microorganisms
- “ Protection of **receiving countries** from import of foreign infesting species

**In goods storage at warehouses:**

- “ Protection of goods from spoilage by animals and microorganisms


**A general (bulk) cargo ship  
bulk carrier, bulk freighter, or bulker**



**BestShippingNew: General arrangement**

Crew accommodation Bulk cargo holds hatch covers  
bulkhead

**A container ship**



**Cargo payload in containers**

**A shipping (intermodal) container**



**Loads may host moulds and other parasites (insects, rodents)**

**40 ft x 8 ft x 8 ft = 2,560 cft**

**A wooden shipping pallet**

**Softwood or hardwood**  
**May host invasive moulds and parasites**

**International Plant Protection Convention:**  
Heat treatment (HT)  
Methyl Bromide treatment (MB)




## The reference source from the FAO



### **E.J. Bond** **Manual of fumigation for insect control**

FAO PLANT PRODUCTION AND  
PROTECTION PAPER 54

First edition 1964

Last revision 1986

<http://www.fao.org/docrep/X5042E/X5042E00.htm>

## critical parameters for effective fumigation schedules

- “ Nature of infestation (type of pest and stage of its life cycle)
- “ Type of fumigant applied
- “ Concentration and distribution of gas
- “ Temperature
- “ Length of time fumigant must be applied
- “ Method by which fumigant is administered
- “ Containment of fumigant
- “ Nature of commodity
- “ Nature of commodity packaging
- “ Monitoring system
- “ Ventilation system

## Types of fumigation

### before loading

- “ In warehouse or storage silos.
- “ In freight containers before loading.

### before sailing

- “ In the hold of the ship with fumigation and ventilation completed.

### fumigation continuing during the voyage (*intransit*)

- “ In the hold prior to sailing
- “ In freight containers before loading

## Rules, regulations and guidelines - 1

- “ **The United Nations International Maritime Organisation (IMO) Safety of Life at Sea (SOLAS) Convention:**

obligation on all Governments to ensure all shipping activities are carried out safely

- “ **The Recommendations on the Safe Use of Pesticides in Ships (IMO Recommendations) (revised 2002):**

a guide to all those involved in the use of pesticides and fumigants on ships and are recommended to governments in respect of their legal obligations under the SOLAS Convention

- “ **The IMO International Maritime Dangerous Goods (IMDG) Code**

## Rules, regulations and guidelines - 2



The screenshot shows the IMFO website with the following content:

- IMFO logo and navigation links: HOME, SITEMAP, JOIN US, CONTACT US
- Quote: "... guaranteed results in accordance with the IMO recommendations ..."
- Section: **The International Maritime Fumigation Organisation (IMFO) Code of Practice (COP)**
- Text: Guidance to fumigators and ships' masters in respect of bagged and bulk cargoes, packaged goods (at: <http://www.imfo.com>)
- Section: **Own requirements of individual countries**
- Text: e.g. US and Canadian Coastguard
- Text: Most countries directly require IMO recommendations to be observed by all vessels in their territorial waters
- Section: **What is fumigation?**
- Text: Fumigation can be most generally defined as the action of releasing and dispersing a toxic chemical that reaches a targeted pest in the gaseous state. The goal of fumigation is to confine enough gas for sufficient time to eradicate the target pest, which in normal conditions is achieved in a static chamber under control of one qualified fumigator, who is able to supervise and eliminate all related processes and possible hazards. Among them is

## Rules, regulations and guidelines - 3

### European Union

#### Fumigation of packaged goods only (freight container fumigation)

Regulation CE 1107/2009

Withdrawal of Directive 91/414/CEE

Superseded with Directives

2008/40/EC, 2006/39/EC e 2003/68/EC.

## Some infestant insects against which fumigation is performed

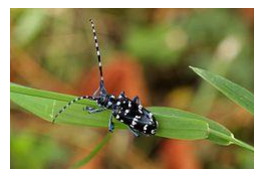
" *Bursaphelencus xylophilus*  
(Pine Wood Nematode)



" *Rhyzoperetha dominica* F.  
(Lesser Grain Borer)



" *Anoplophora chinensis*  
(Citrus Longhorn Beetle, CLB)



## List of chemicals examined in the FAO Manual

" **Methyl bromide** →

" **Phosphine** →

" Hydrogen cyanide (HCN)

" Ethylene dibromide

" Ethylene oxide

" Ethylene dichloride

" Carbon disulphide

" Carbon tetrachloride

" Chloropicrin

" Dichlorvos (DDVP)

" **Sulphuryl fluoride** →

" Acrylonitrile

" Minor fumigants

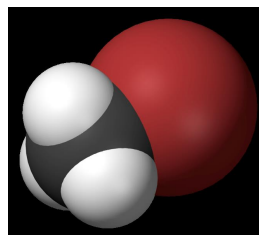
**Of a current  
interest**

**potential  
interest**

**(Carbonyl sulphide)  
Nitrogen gas («inertization»)**

## Methyl bromide - 1

- “Also a natural product of marine organisms
- “Ozone depletor (Montreal 1992)
- “Regulated substance
- “Phased out in 2005
- “Exemption for critical applications
- “Effective concentration 48 g/m<sup>3</sup> (13,000 ppm)
- “Safe concentration < 5 ppm



## Methyl bromide - 2

### Phaseout according to Montreal Protocol

1993 to 1998	Freeze at 1991 baseline levels (U.S. Consumption ~25,500 Metric Tons) (consumption = production + imports - export)
1999 to 2000	25% reduction from baseline levels
2001 to 2002	50% reduction from baseline levels
2003 to 2004	70% reduction from baseline levels
2005	100% phase out -except for allowable exemptions such as critical use exemptions agreed to by the Montreal Protocol Parties

## Methyl bromide - 3

### Critical Use Exemption (USA)

Strawberry Fruit	Moderate to severe black root rot or crown rot Moderate to severe yellow or purple nutsedge infestation Moderate to severe nematode infestation Local township limits prohibiting 1,3-dichloropropene
Food Processing Rice mills Pet food manufacturing Walnuts, plums, figs, Å	Moderate to severe beetle, weevil, or moth infestation Presence of sensitive electronic equipment subject to corrosion Rapid fumigation
Dry Cured Pork Products	Red legged ham beetle infestation Cheese/ham skipper infestation Dermestid beetle infestation Ham mite infestation

### Quarantine and Preshipment (QPS) Exemption

- i. Official control is that performed by, or authorized by, a national plant, animal, or environmental protection or health authority;
- ii. quarantine pests are pests of potential importance to the areas endangered thereby and not yet present there, or present by not widely distributed and being officially controlled; e.g., khapra beetle (*Trogoderma granarium* Everts)

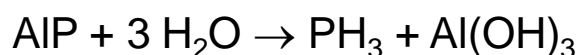
## Phosphine (generating chemicals) - 1

- “ Phosphine (PH<sub>3</sub>)
- “ Extremely flammable gas, explosive
- “ Heavier than air (1.34 g/L)
- “ Lung toxic, haemotoxic in mammals
- “ Occupational exposure limits (EU)
- “ 8 hours limit value: 0,14 mg/m<sup>3</sup> (0,1 ppm)
- “ Short term limit value: 0,28 mg/m<sup>3</sup> (0,2 ppm)



## Phosphine (generating chemicals) - 2

“Generated from reaction of  
Aluminium - Magnesium - Zinc phosphide  
with moisture water



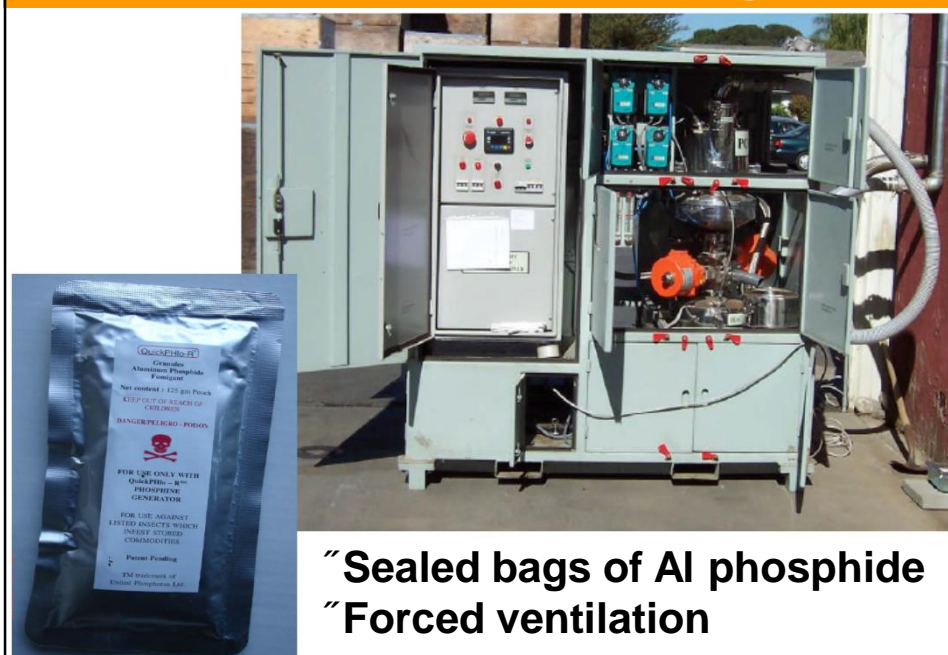
“Pre-packaged chemicals (tablets, granules)

“«*The Tablets Of Love*» → suicidal use

“Mixture with  $\text{CO}_2$  improves diffusion

“Commercial devices for generation and  
diffusion of phosphine gas

## Generation of phosphine gas



“Sealed bags of Al phosphide  
“Forced ventilation

## Sulphuryl fluoride - 1

- “ High-density gas (4.1 g/L)
- “ Odorless, colorless, non-reactive
- “ Long atmospheric half-life (30-40 yr)
- “ Strong greenhouse effect
- “ Low water solubility (750 ppm @ 25°C pH 7)
- “ Facile hydrolysis (mineralization) in water

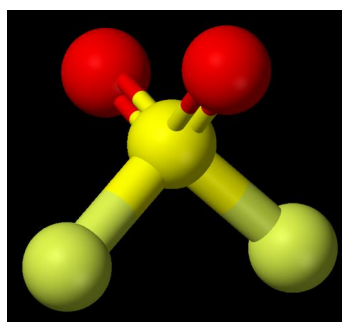
### Toxicity:

- “ LC<sub>50</sub>: 3020-3730 ppm (1-hour, rat)
- “ Very few cases of human fatal intoxication
- “ no reproductive, teratogenic, or mutagenic effects

## Sulphuryl fluoride - 2

- “ Commercial brand names:

- . *Vikane* (Dow)
- . *Zythor* (Ensystem)
- . *ProFume* (Dow)
- . *Master Fume* (Drexel)



- “ Application doses
- “ max: 1,500 g h/m<sup>3</sup> for warehouses
- “ AOEL: 3 ppm (12,6 mg/m<sup>3</sup>)
- “ Measurement with Fumiscope (TCD)

## Methods for fumigation

### Holds

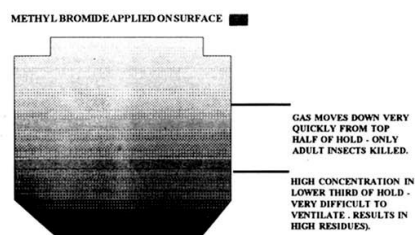
- “Critical penetration by diffusion into the mass of hold content
- “Forced recirculation of gas
- “Purging of gas below safe levels before opening of hatches

### Containers

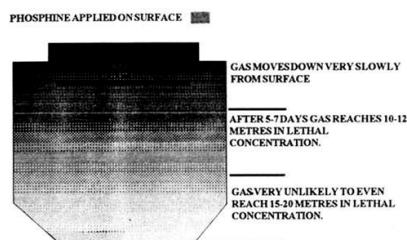
- “Penetration depends on the nature of load
- “Fumigators still in place at container opening
- “Labelling - warning
- “Localized aspiration of container air

## Penetration in hold depends on critical physical properties of gas

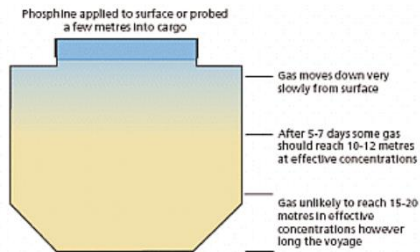
“MeBr *much* (3-5 times) heavier than air



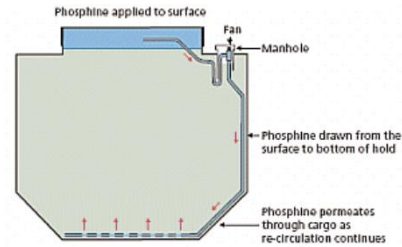
“PH<sub>3</sub> *not sufficiently* heavier than air



## Hold fumigation

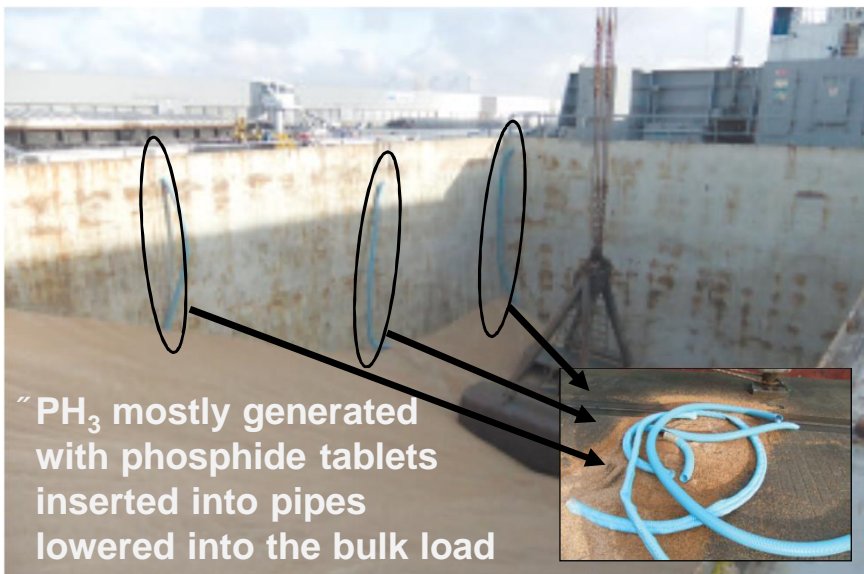


“Solid phosphide (tablets) placed on the surface, covered with a few metres of cargo and left to react with residual humidity




“Gas released from phosphide forced by a fan into the depth of the cargo and allowed to penetrate into the bulk by diffusion

## Hold fumigation



### Hold fumigation


**Before unloading**



DPI

purging

ventilator





Gas detector (Dräger)


Check of residual gas concentration

### Container fumigation - 1

“ encapsulation

“ **Protect workers with DPIs**



	MeBr	PH <sub>3</sub>	SO <sub>2</sub> F <sub>2</sub>
IDLH (ppm)	2000	200	1000
OEL TWA;STEL (ppm)	5; 15	0.1; 0.2	5; 10
Filter code (3M)	AX	SA	SA

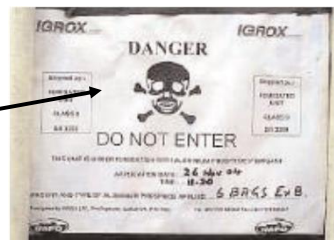
**Equivalent to OSHA coding «brown»**  
for Acid gases, organic vapors, and ammonia gases

## Container fumigation - 2

“ treatment

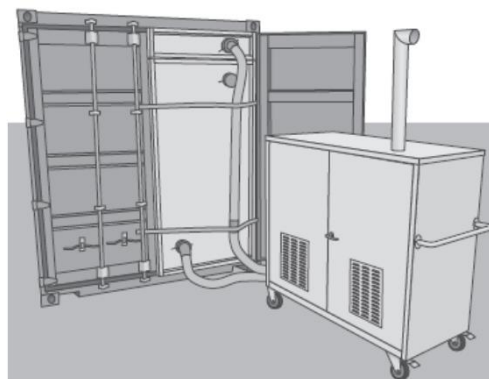
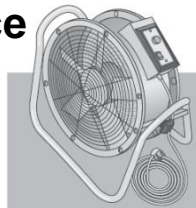


“ warning



## Container fumigation - 3

“ clearance



“ measurement




“ Reactive tubes  
“ Gas monitors

## Assessment of exposure

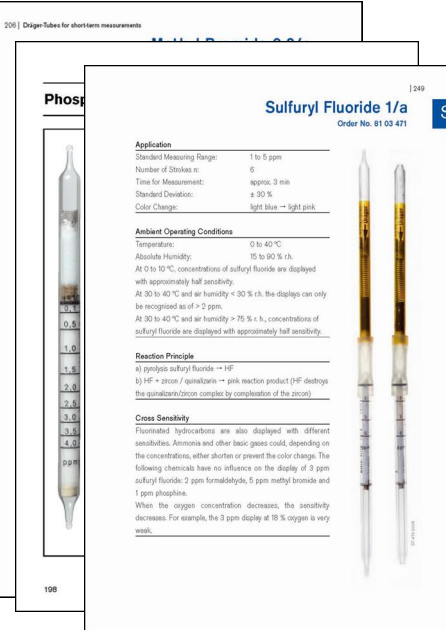
**Dräger indicator tube for:**

- “ **methyl bromide**  
range 0.2 - 2 ppm vs.  
8-hrs TLV-TWA : 5 ppm
- “ **Phosphine**  
LoD 0.1 ppm vs.  
8-hrs TLV-TWA : 0,1 ppm  
TLV-STEL: 0,2 ppm
- “ **sulphuryl fluoride**  
range 1 - 5 ppm vs.  
AOEL: 5 ppm

Dräger-Tube with built-in reagent ampoule (content is granular preparation)



Dräger-Tube with built-in reagent ampoule



208 | Dräger-Tubes for short-term measurements

Phosphine

Sulphuryl Fluoride 1/a  
Order No. 81 03 471

Application

Standard Measuring Range: 1 to 5 ppm  
Number of Strokes: 6  
Time for Measurement: approx. 3 min  
Standard Deviation: ± 30 %  
Color Change: light blue → light pink

Ambient Operating Conditions

Temperature: 0 to 40 °C  
Absolute Humidity: 15 to 90 % r.h.  
At 0 to 10 °C, concentrations of sulphuryl fluoride are displayed with approximately half sensitivity.  
At 30 to 40 °C and air humidity < 50 % r.h. the displays can only be recognized as of > 2 ppm.  
At 30 to 40 °C and air humidity > 75 % r.h., concentrations of sulphuryl fluoride are displayed with approximately half sensitivity.

Reaction Principle

a) pyrolysis sulphuryl fluoride → HF  
b) HF + zinc / quinoline → pink reaction product (HF destroys the quinoline/zinc complex by completion of the zinc)

Cross Sensitivity



Fluorinated hydrocarbons are also displayed with different sensitivities. Ammonia and other basic gases could, depending on the concentrations, either shorten or prevent the color change. The following chemicals have no influence on the display of 3 ppm sulphuryl fluoride: 2 ppm formaldehyde, 5 ppm methyl bromide and 1 ppm phosphine.  
When the oxygen concentration decreases, the sensitivity decreases. For example, the 3 ppm display at 15 % oxygen is very weak.

198

## Assessment of exposure

**Gas detectors:**

- “ **MIRAN infrared**
- “ **Fumiscope (TCD)**

## Health issues for operators

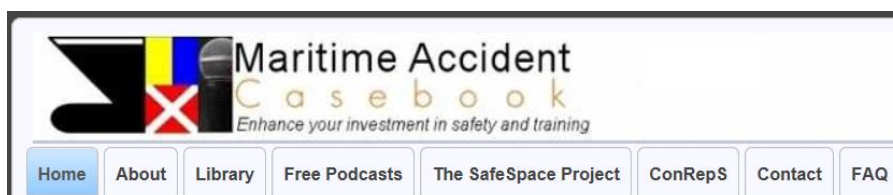
- “ Exposure during fumigation
- “ Exposure during shipping
- “ Exposure during unloading/inspection

## Health issues for population

- “ Exposure after fumigation

## Source of accidents reporting

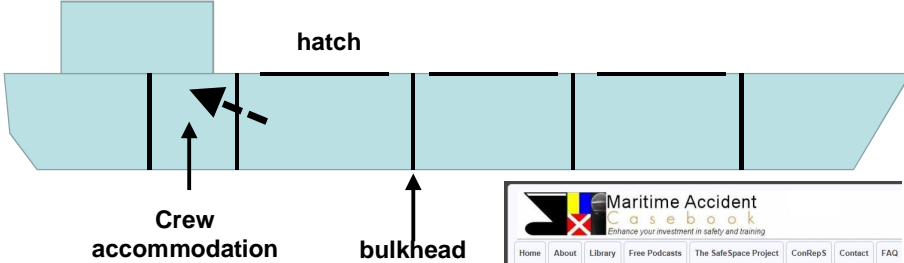
***<http://maritimeaccident.org/>***



«fumigation» yields 31 results



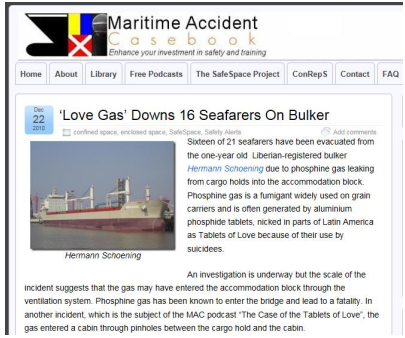
## Exposure accidents occurred during shipping



**Reported cases of intoxication of crew from diffusion of fumigants through leaky bulkheads**

### Phosphine leak in crew block

**A full crew in danger**  
In 2000 an issue of the US Coast Guard News informed that a bulk carrier bound for Australia had to seek refuge at Coos Bay, Oregon due to the entire crew being affected by gas emitting from cargo hold No. 6. That hold contained soya bean meal, and was one of three holds fumigated to control insects at Port Angeles, Washington.



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**'Love Gas' Downs 16 Seafarers On Bulker**  
Sixteen of 21 seafarers have been evacuated from the one-year old Liberian-registered bulker *Hermann Schoening* due to phosphine gas leaking from cargo holds into the accommodation block. Phosphine gas is a fumigant widely used on grain carriers and is often generated by aluminium phosphide tablets, nicked in parts of Latin America as Tablets of Love because of their use by suicides.

An investigation is underway but the scale of the incident suggests that the gas may have entered the accommodation block through the ventilation system. Phosphine gas has been known to enter the bridge and lead to a fatality. In another incident, which is the subject of the IMAC podcast 'The Case of the Tablets of Love', the gas entered a cabin through portholes between the cargo hold and the cabin.

## Exposure accidents involving clandestine emigrants

May 29 2008 **Stowaways – A Deadly Business**  
Uncategorized Add comments

Two communications arrived in MAC's inbox over the past couple of days with bad news for the families of four now-dead stowaways.

**Two bodies were found in a hold** aboard the bulk carrier *Pascal* in Ayr, Scotland. The two men apparently boarded the vessel in Tunisia and hunkered down in a phosphate filled hold with a single bottle of water between them on or around 15th May before the hatches were sealed. Their bodies were discovered on 26th May, eleven days later.

**The death of a stowaway**  
Stowaways trying to flee a country may do so in desperation, but may not know the dangers to which they expose themselves – and certainly not when they hide in cargo holds under fumigation. Six stowaways were found on board a vessel in 2009, after leaving Lagos, Nigeria. The first one was found inside a cargo hatch, when a crew member heard him banging on the steel. Two more were found in another hold and two came out of the garbage bin. Those having been in the cargo holds were very weak and groggy, but recovered by resting in fresh air. The sixth was not so lucky; he was found on the upper platform of

## Odd circumstances ... at home

[J Appl Toxicol](#), 1996 Sep-Oct;16(5):445-8.

**Fatal accident resulting from methyl bromide poisoning after fumigation of a neighbouring house; leakage through sewage pipes.**

[Langård S<sup>1</sup>](#), [Rognum T](#), [Fløttered O](#), [Skaug V](#).

[Author information](#)

### Abstract

An intoxication after using methyl bromide (CH<sub>3</sub>Br) in fumigation is reported. The accident resulted in the death of a newborn infant within 12-13 h after exposure, as well as clinical intoxication of the infant's parents. The concentration of bromide ion in the infant's blood was 170 mg l<sup>-1</sup> and in the parents blood it was 130 and 110 mg l<sup>-1</sup>. Autopsy showed that the cause of death was acute pneumonia due to aspiration, most likely resulting from vomiting and aspiration after inhalation of CH<sub>3</sub>Br. The clinical symptoms of the parents are reported, as well as a brief survey on the kinetics and CH<sub>3</sub>Br toxicity in animals and humans. Reconstruction of the events prior to the intoxication revealed that the sewage pipes serving the two houses had been sucked empty only 1-2 h prior to the start of fumigation, resulting in an open sewage connection between the houses and permitting CH<sub>3</sub>Br to leak from the treated house into the house of the affected family.

PMID: 8889797 [PubMed - indexed for MEDLINE]

## Final considerations

- “Use of fumigation will continue in the future
- “Potential for primary prevention
  - “Increased use of less toxic chemicals
  - “Inertization with nitrogen → explosion safety
- “Awareness in peripheral countries
- “Harmonization of regulations in peripheral countries
  - “Prior Informed Consent
  - “FAO Pesticide Registration Toolkit (in preparation)

**Thanks for  
attention**

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