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## Measuring new fumigants with Dräger-Tubes®

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For more than 60 years, Dräger Safety has offered the well-known Dräger-Tubes®. The detection of gases and aerosols is the main focus with this system. Today, Dräger Safety offers more than 220 different tubes.

The Dräger Tubes® program works in an easy way, combining a precise pump with a glass tube filled with analytical chemicals. The measurement is made by drawing a definite volume of sample gas through the tube. Immediately after the measurement is finished, the concentration of the measured gas can be read on the detection layer of the tube. The chemical reaction inside the tube has left an easy-to-read stain.

The detection of fumigants is one of the most interesting markets for Dräger-Tubes® (Table 1). Because of constraints and the decreased use of older products, new fumigants have to be developed for the future. Otherwise, a profitable production of crops, fruits and other plants is not possible.

A couple of new gases have received approval in several different countries. But only a cost efficient detection system helps to optimise the fumigation process.

Dräger Safety has focused on the development of new tubes for these gases.

The first tube of this project was to develop a new tube for Methyl Bromide, giving an answer to a new threshold limit value in Europe of 0.5 ppm. The new Draeger Tube Methyl Bromide 0.2/a covers this new limit with its detection range 0.2 – 8 ppm. It shows not cross sensitivities

to other fumigants, except Ethylene Dibromide. This gas will be detected with the same sensitivity.

**New Dräger-Tube® for Sulfuryl Fluoride**

This tube provides a measuring range of 1-5 ppm of Sulfuryl Fluoride. No cross sensitivities to other fumigants. A high temperature inside the tube cracks the molecules and the fragments can be detected specifically to the detection layer.

**New Dräger-Tube® for Chloropicrin**

A very low measuring range of 0.1-2 ppm covers the threshold limit value. There are no cross sensitivities to other fumigants.

A brand new Draeger Tubes is designed for detection of Ethyl Formate. The TLV of 100 ppm worldwide is covered by a measuring range of 20-500 ppm. This tube shows no cross sensitivity to CO or CO<sub>2</sub>. The detection of Vapormate® is possible.

## Fumigation of freight containers

### General

Fumigation of goods like grain, wood, coffee, textiles and many other organic / biological materials were practiced since decades. In correlation with the increasing use of freight container for the export of all kinds of goods the market of fumigation is continuously increasing. Often fumigation is practiced for prophylaxis with the goal to save the transporting goods and also to inhibit the migration of varmints

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**Table 1.** All other Dräger-Tubes® for fumigants in an overview.

Name	Order number	Measuring range
Phosphine 0.01/a	81 01611	0.01 to 1 ppm
Phosphine 0.1/a	CH 31101	0.1 to 4 ppm
Phosphine 1/a	81 01801	1 to 100 ppm
Phosphine 25/a	81 01621	200 to 10,000 ppm
Phosphine 50/a	CH 21201	50 to 1,000 ppm
Methyl Bromide 0.2/a	8103391	0.2-8 ppm
Methyl Bromide 0.5/a	81 01671	0.5 to 30 ppm
Methyl Bromide 3/a	67 28211	3 to 100 ppm
Methyl Bromide 5/b	CH 27301	5 to 50 ppm
Sulfuryl Fluoride 1/a	8103471	1-5 ppm
Chloropicrin 0.1/a	8103421	0.1-2 ppm
Ethyl Formate 20/a		20-500 ppm

worldwide.

The worldwide transport of freight containers results in 3,000,000 of freight containers arriving the harbour of Rotterdam, Netherlands.

This big mass of containers have to be seen to a big percentage as transit goods. They are feedered to smaller harbours. So the risks of the fumigants are shifted also into the inshore harbours, trucks and trains and last to the address of the particular container.

The safety risks are that the fumigants are extremely toxic or lethal toxic not only to the varmint, which have to be killed, but also for the workers which come into contact with the containers and the transported goods.

First accidents with severe consequences for the health of the workers are pointing to the brisance of this worldwide problem.

This situation intensifies with the fact that the labelling of fumigated freight containers is very insufficient though there are international duties.

It often seems that during offshore transport of containers higher requirements have to be fulfilled. This leads to higher transport costs. So the labelling will be forgotten to save money.

Another problem is that during the fumigation process in the exporting country too big masses of fumigants were impregnated into the container.

Because of that it is possible that also accidents can happen at a well labelled container and after perfect ventilation, when the addressee opens the container. The reason for that are residues of fumigants can evaporate out of the transporting goods.

A study of the dutch ministry (VROM, 2002) shows that of the 3,000,000 container arriving Rotterdam, Netherlands, 1,000,000 are fumigated. But only 3 % of these are labelled correctly.

This 97 % are an enormous potential of permanent safety risk which does not only during feeder transport with ships, trucks and trains, but also at the addressees reach in this condition.

Because of this situation actions are initialized worldwide by the regulating authorities of the countries.

For example there are regulations for the import of wood packaging material, for example in Australia, New Zealand, Argentina, Brazil, China, Canada, USA and Mexico. The allowed

methods are boiler pressure impregnation, heating treatment or fumigation with different fumigants like Methyl Bromide or Sulfuryl Fluoride.

The type of fumigant depends on the condition of the transporting goods.

Measurement of concentrations of fumigants in freight containers

Well established fumigants in the market of freight containers are e.g.:

Nitrogen (N<sub>2</sub>), Ammonia (NH<sub>3</sub>), Methyl Bromide (CH<sub>3</sub>Br), Hydrocyanic Acid (HCN), Phosphine (PH<sub>3</sub>), Formaldehyde (HCHO), Chloropicrine (CCl<sub>3</sub>NO<sub>2</sub>), Ethylen Oxide (C<sub>2</sub>H<sub>4</sub>O), Carbon Dioxide (CO<sub>2</sub>), Carbon Monoxide (CO), Sulfurylfluoride (SO<sub>2</sub>F<sub>2</sub>), Ethylen Dibromide(C<sub>2</sub>H<sub>4</sub>Br<sub>2</sub>).

The variety of fumigants raises the question: How is it possible to detect fumigants looking on maximum safety and acceptable costs?

These measurements consist of checking the concentration during the fumigation, observation of the threatened workers and the clearance measurement of the container after delivery to the addressee and performed ventilation.

The issue of a clearance measurement becomes more critical as mentioned above that after the ventilation the fumigants start to evaporate out of the transporting material and the niches caused by piling of stock.

The fumigation with phosphine is performed with pills of Phostoxin® which are placed into the freight containers floor. These pills consist of aluminium phosphide. This material will react with water (humidity) and releases the toxic phosphine. Very often too much of the pills are placed in the containers. This causes a continuous production of phosphine which will stop when a saturation point is reached. But when opening the doors or starting the ventilation of the container, the chemical reaction will start again. But a clearance measurement before opening the container will give a wrong reading. The safety way is to ensure the removal of the resisting pills before emptying the container. This is very often difficult because the pills were thrown into the container packed into linen bags or socks.

These are difficult to locate in the containers. The fumigation continues and is a potential risk for the workers.

### **Test kit for observation of fumigants in freight containers**

The brand-new “fumigation box” of Draeger Safety AG & Co KG aA Germany enables a quick and easy measurement of the concentration of fumigants in the freight containers. The content of this box is designed for non chemicians or non analysers, that well educated workers are able to perform this measurement.

The content consist of the Draeger Handpump Accuro®, a special bar probe for freight containers and specific Draeger tubes which offers the user a fast and easy measuring option.

Normally the measurements at freight containers are executed at a still closed and sealed container. This ensures that:

- the real existing concentration of fumigant is monitored and,
- the burden of the health of the workers is reduced to minimum.

It is recommended to use the Draeger bar probe for containers, pushing it through the sealing rubber lips of the container doors. Also it is possible to drill holes into the containers exterior shell.

The procedure depends on the local country regulations of the importing country. Australia for example demands to take the sample at drilled holes. The robustness of the Draeger Bar probe allows both ways of sample taking. In the Draeger fumigation box is included a measuring strategy for measurements in fumigated freight containers.

The following procedure is recommended:

- The fumigant in the freight container is well known because of labelling. In this case evaluation of draeger tubes depends on the labelled gas (Table 2).
- Unknown fumigants are in the container. The container is not labelled, but suspicious to be fumigated. In this case the use of the Draeger Simultantest is the right decision. There are two kinds available for fumigation.

**Table 2.** Evaluation of Draeger tubes.

Fumigation-Gas	Draeger-Tube	Part Nr	Measuring Range
Ammonia (NH <sub>3</sub> )	Ammonia 5/a	CH 205 01	5 - 700 ppm
Hydrocyanic Acid (HCN)	Hydrocyanic Acid 2/a	CH 257 01	2 – 30 ppm
Formaldehyde (HCHO)	Formaldehyde 0,2/a,	67 33 081	0,2 – 5 ppm
Methyl Bromide (CH <sub>3</sub> Br)	Methylbromide 0,5/a	81 01 671	0,5 – 30 ppm
	Methylbromide 0,2/a	81 03 391	0,2 – 8 ppm
Phosphine (PH <sub>3</sub> )	Phosphine 0,1/a	CH 311 01	0,1 – 4 ppm
	Phosphine 1/a	81 01 801	1 – 100 ppm
	Phosphine 25/a	81 01 621	25 – 10,000 ppm
Chloropicrin (CCl <sub>3</sub> NO <sub>2</sub> )	Chloropicrin	81 01 421	0,2 – 2 ppm
Ethylene Oxide (C <sub>2</sub> H <sub>4</sub> O)	Ethylene Oxide 1/a	67 28 961	1 – 15 ppm
Carbon Dioxide (CO <sub>2</sub> )	Carbon Dioxide 0,1%/a	CH 235 01	0,1 – 6 Vol%
Carbon Monoxide (CO)	Carbon Monoxide 10/b	CH 206 01	10 - 3,000 ppm
Sulfuryl Fluoride (SO <sub>2</sub> F <sub>2</sub> )	Sulfuryl Fluoride-Test	81 03 361	5 – 10 ppm

a) Draeger Simultantest Fumigation 8103340:

Ammonia (NH<sub>3</sub>)

Hydrocyanic Acid (HCN)

Formaldehyde (HCHO)

Methyl Bromide (CH<sub>3</sub>Br)

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

b) Draeger Container Fumigation Set 1:

Hydrocyanic Acid (HCN)

Formaldehyde (HCHO)

Methylbromid (CH<sub>3</sub>Br), Ethylene

Dibromide (C<sub>2</sub>H<sub>4</sub>Br<sub>2</sub>)

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

Ethylene Oxide (C<sub>2</sub>H<sub>4</sub>O)

These Simultantest are detecting that above mentioned fumigants in the range of its threshold limits. If there is no positive reading with this sets visible, the measurements have to be continued with the tubes at Table 3.

**Table 3.** Draeger tubes for gas detection.

Fumigation-Gas	Draeger-Tube	Part Nr	Measuring Range
Ammonia (NH <sub>3</sub> )	Ammonia 5/a	CH 205 01	5 - 700 ppm
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	Methylbromide 0,2/a	81 03 391	0,2 – 8 ppm
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Carbon Monoxide (CO)	Carbon Monoxide 10/b	CH 206 01	10 - 3,000 ppm
Sulfuryl Fluoride (SO <sub>2</sub> F <sub>2</sub> )	Sulfuryl Fluoride-Test	81 03 361	5 – 10 ppm

## Results and consequences

If the presence of a fumigant and the concentration above a threshold are fixed, the freight container has to be ventilated in accordance with country specific regulations. After that the freight container has to be sealed again and the concentrations have to be checked again (Figure 1).

The issue of fumigated freight containers is discussed. It is mentioned the big variety of fumigants and its consequences in the field of measurements of concentrations and of clearance measurements. A simple kit of measuring devices is shown which enables these measurements of concentrations and clearance.

A new application for our tubes is the testing

of fumigated transport containers. There are strong regulations for the fumigation of containers in the worldwide shipping of goods in order to protect the importing countries from foreign varmint.

After the fumigation process in the exporting harbour, the containers are purged with fresh air and a certificate confirms the process. No labelling is required. But depending on the goods placed inside the containers, an amount of fumigant stays inside.

Harbour workers, truckers and customs people who have to open the containers for inspection may come into contact with significant concentrations of fumigants. Dräger Safety has created two sets of tubes for a fast and simultaneous check to reduce the risk of an exposition (Table 4).

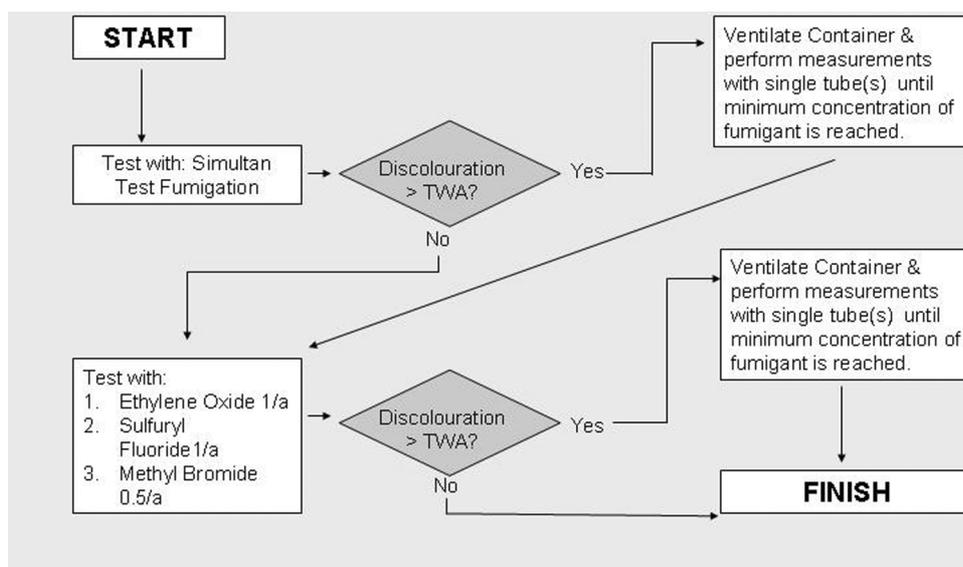


Figure 1. Strategy to detect unknown fumigants.

Table 4. Future developments for the next Dräger-Tube®: MITC, Carbonyl Sulfide, and Dicyanide.

Name	Part number	Detectable gases	Measuring time
SimultanTest Fumigation	8103410	Formaldehyde Methyl Bromide Phosphine Hydrocyanic acid Ammonia	3 minutes
SimultanTest Container Fumigation I	8103380	Formaldehyde Methyl Bromide Phosphine Hydrocyanic acid Ethylene Oxide	4 minutes

## References

VROM, 2002. Measuring the amount of gas in

import containers. Ministry of Housing, Spatial Planning and the Environment, Netherlands. T. Knol-de Vos.