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Gasmet™ FTIR application note

Container Fumigation

KEY WORDS

- Container
- Fumigation
- Fourier Transform Infrared (FTIR)
- Fumigant
- Ventilation
- Pest animals
- Library Search Tool

PRODUCTS

- DX4040 Portable FTIR Gas Analyzer
- Calcmet 4040 Professional Analytical software package

OVERVIEW

Sea cargo containers often contain hazardous levels of gases and vapors which are dangerous for the people working in inspection, loading and unloading. These gases are **either fumigants or are arising from the packaging materials and goods**. Some of the containers and wooden packaging materials may contain pest animals and micro-organisms, so they need to be fumigated in order to avoid the spreading of invasive species and diseases. After fumigation the containers should be labeled with proper **warning signs**, (Figure 1) so that they are ventilated before opening.

Figure 1. Warning sign on container during fumigation.

However, absence of marking cannot be taken to mean fumigants are not present. Containers marked as having been ventilated after fumigation may also contain fumigants that were absorbed by the cargo and released during transit.

Some products shipped in containers may release VOCs, for example, from solvents and glues used in manufacturing processes, in which case the concentrations of toxic gases may increase to significantly high levels in the confined space of the container. Generally, it is necessary

for measurements to be taken by customs inspectors, as **a health and safety precaution**. Usually, customs staff select the containers to be measured based on factors such as the country of origin of the container, the products inside the container and arrangements between producers and suppliers.

While most containers originate in China and Southeast Asia, cargo container measurements take place in ports across the world, because the same gases are encountered in all ports. The idea of the measurement is to screen the toxic containers from the clean containers and to ensure that the containers can be opened without harm. "**Clean container**" means that all the concentrations of measured gases are below the occupational exposure limits whereas "**toxic container**" means there is at least one component above the limit. In many cases the shipping companies are responsible for performing the analysis.

THE BIGGEST CHALLENGES IN CONTAINER MEASUREMENTS

There are several international and national recommendations and instructions, e.g. by IMO (International Maritime Organization) and FAO (Food and Agriculture Organization) of the United Nations, which prescribe how the fumigation should be performed. These recommendations mainly focus on the safety issues and give guidelines on how the fumigation/ventilation-procedure can be improved. They do not specify the type or specifications of the monitoring equipment that should be used.

The occupational exposure limits that determine the maximum acceptable concentration levels of certain substances, can vary significantly between different countries. For example, α-Pinene is a chemical arising from wooden packaging materials, having a pleasant odor but classified as a hazardous substance. It has a TLV (threshold limit value) of 20 ppm in Belgium and in Canada-Ontario, and 25 ppm in Sweden, but in the other countries there is no limit value for this compound (Source: GESTIS Open Database).

In some countries the law prescribes the amount of gases to be measured, e.g. in the Netherlands the minimum number of compounds is 18. In practice this leads to a situation where organizations base their safety analyses on a narrow, unreliable set of measurements, in which only a small fraction of all the existing gases is analyzed. In addition, some instruments give false negatives due to a lack of gas calibration, resulting in hazardous situations if containers with high levels of toxic gases are opened without ventilation.

GASMET FUMIGATION APPLICATION AND DX4040 SPECIFICATION

Gasmet DX4040 FTIR (Fourier Transform Infrared) gas analyzer is used for container measurements to measure fumigants and other emitted gases (Figure 2). The **battery powered** backpack-size analyzer records infrared spectra at 10 scans/s and is capable of sub-ppm detection. The DX4040 requires **no span gas calibrations** and only a short zero procedure needs to be undertaken before measuring.

The analyzer is controlled by a standard laptop computer or a rugged PDA (Personal Digital Assistant) which allows simultaneous analysis of 25 different gases. When operating by laptop PC, the DX4040 is able to perform the **simultaneous analysis of up to 50 gases** (Table 2). The FTIR measurement principle allows the determination of both inorganic and organic substances regardless of their molecular weight.

Figure 2. Portable Gasmet DX4040 for container measurements.

The 50 gas library is configured to include all common fumigants and a wide range of substances released from cargo. Cross-interferences between gases is automatically taken into account in the analysis settings for each compound. Calcmet 4040 Professional software is used to control the analyzer and display the results. The results produced can be traced back to the original infrared spectra of the samples, and a built-in QA/QC routine ensures reliable results. The technical specifications and key characteristics of portable DX4040 FTIR gas analyzer are collected in Table 1 below.

Table 1. Technical details of DX4040 FTIR gas analyzer.

	DX4040
Cell Temperature (controlled)	Ambient
Built-in sample pump	1.5 l/min
Water vapor (V/V%)	0 – 3 %
Sample cell volume	400 mL
Operating time (Bluetooth ON)	2.5 h
Interface	PDA or External computer via RS-232C cable
Software	Calcmet Software with DX4040 Pro key

Table 2. Typical gases with measuring ranges for container application.

Compound Name	Range	Unit	Compound Name	Range	Unit
Water	0 – 3	vol-%	Ethane	0 – 50	ppm
Carbon Dioxide[8]	0 – 2000	ppm	*n*-Propane	0 – 50	ppm
Carbon Monoxide[1+8]	0 – 200	ppm	*n*-Butane	0 – 50	ppm
Nitrous Oxide	0 – 100	ppm	*n*-Hexane	0 – 50	ppm
Methane	0 – 100	ppm	*n*-Octane	0 – 50	ppm
Nitrogen Monoxide	0 – 200	ppm	Isopentane[3]	0 – 50	ppm
Ammonia	0 – 50	ppm	Ethylene (Ethene)	0 – 50	ppm
Formaldehyde[2+8]	0 – 50	ppm	*n*-Propene	0 – 50	ppm
Ethylene Oxide[7+8]	0 – 50	ppm	Cyclohexane[4]	0 – 50	ppm
Benzene[4]	0 – 50	ppm	α-Pinene[2]	0 – 50	ppm
Toluene[4]	0 – 200	ppm	β-Pinene[2]	0 – 50	ppm
Ethyl Benzene[4]	0 – 100	ppm	3-Carene[2]	0 – 50	ppm
m-Xylene[4]	0 – 200	ppm	Limonene[2]	0 – 50	ppm
o-Xylene[4]	0 – 200	ppm	Formic Acid[1]	0 – 50	ppm
p-Xylene[4]	0 – 200	ppm	Acetic Acid[1]	0 – 50	ppm
Methyl Bromide[8]	0 – 200	ppm	Methyl Acetate[6]	0 – 50	ppm
1,2-Dichloroethane[3]	0 – 200	ppm	Ethyl Acetate[6]	0 – 50	ppm
Chloropicrin[8]	0 – 20	ppm	2-Butoxyethyl Acetate[6]	0 – 50	ppm
Styrene[5]	0 – 200	ppm	Dimethoxy Methane	0 – 50	ppm
Phosphine[8]	0 – 50	ppm	Acetaldehyde[1]	0 – 50	ppm
Sulfuryl Fluoride[8]	0 – 50	ppm	Methyl Ethyl Ketone[6]	0 – 50	ppm
Hydrogen Cyanide[8]	0 – 50	ppm	Methanol[1]	0 – 200	ppm
Carbon Disulfide[8]	0 – 200	ppm	Ethanol[1]	0 – 200	ppm
Acetone[4]	0 – 200	ppm	Isopropanol[6]	0 – 50	ppm
Dichloromethane[3+8]	0 – 200	ppm	Ethylene Dibromide[8]	0 – 50	ppm

[1)] Foodstuff, [2)] Wood and plywood shipping materials, [3)] Refrigerant; kitchenware, A/C units, [4)] Solvents, plastic goods, [5)] Rubber shoes, tires, [6)] Inks, printed materials, [7)] Medical supplies, [8)] Fumigant

MEASUREMENT TECHNIQUE

The measurement of air quality inside a container takes some time and the procedure may cause delays, which in turn increases costs. In order to save money and time, the target is therefore to employ an analyzer which measures as many toxic gases as possible, as fast as possible, and still gives reliable results. It is important to minimize “false positives“, since each wrong result causes unnecessary work and creates extra costs. However, experience has shown that “false positives” are considered to be more acceptable than “false negatives” which can result in a lethal threat to employees opening the container.

The gas composition inside a container can be measured by the Gasmet DX4040, which gives the results in three minutes. Some organizations measuring multiple containers per day use 2 x 1 minute measurement time and a flushing time of 30 seconds. If no toxics are present, the container is moved on normally. On the other hand, if the analyzer measures concentrations over TLV the container is re-analyzed, after which the ventilation procedure is started. The container is ventilated for as long as the concentrations are below occupational exposure limits. Degassing of the container may take from hours to weeks depending on the type of toxic gases, size of container and the products inside the container.

In general, the measurement techniques and the equipment used, vary between countries, ports and the organizations responsible for measurements.

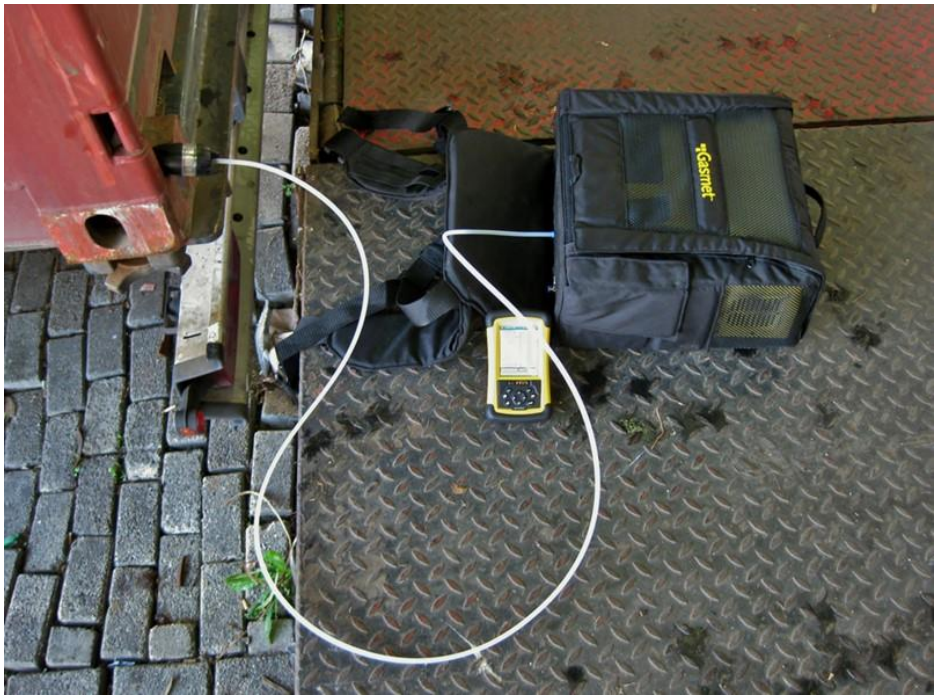

Figure 3. Gasmet gas analyzer measuring gases inside a container.

ADVANTAGES OF FTIR IN FUMIGATION MEASUREMENTS

The DX4040 performs simultaneous analysis of up to 50 gases with **compensation for cross-interference effects**. This is one of the greatest advantages of the Gasmet DX4040 because it significantly reduces the risk of accidents. Moreover, the high amount of gases measured in a short time enables the user to **measure many containers per day** with a single analyzer, which reduces costs since there is no need to buy several detectors or sensors for different gas compounds.

Another major advantage is the **minimal amount of calibration and maintenance necessary**. High concentrations of toxic gases do not harm FTIR and the instrument can recommence analysis after a 30 second backflushing. Moreover, it does **not require sample preparation** and it does **not produce hazardous waste**, as is the case with the chemical stain tubes.

There are many different toxic gases that may be present inside a container and it is difficult to say which components are the most common. Many of the analyzers, detectors and sensors on the market are able to measure certain toxic gases, and they only give the concentration results for the selected compounds. In contrast, Gasmet's Calcmet Pro Software enables the **identification of unknowns** (gases which are not included in the component list of the fumigation application) by using the **Library Search Tool**. There are more than 250 gases in the Gasmet reference library and over 5000 gases in the NIST Library.

The DX4040 is also user-friendly, since it is light-weight, easy to carry and the running of the software does not necessarily require a highly qualified technician. FTIR technology represents a good balance of sensitivity and **the ability to cope with a complex gas matrix**.