Rijksinstituut voor Volksgezondheid en Milieu

LETTER REPORT

INDICATIVE MEASUREMENT CAMPAIGN TO DETERMINE THE PRESENCE OF GASEOUS BIOCIDES IN OCEAN SHIPPING CONTAINERS IN THE ROTTERDAM HARBOUR AREA ON 26 AND 27 APRIL 2001

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1. INTRODUCTION

From the containers that enter or leave the Netherlands via the Rotterdam harbour, the customs office selects a small number that are subjected to a "container scan". If the scanning images give reason to do so, the customs office can open the container and inspect the contents. Before conducting the inspection, the customs office commissions a fumigation company to take measurements in the container for the presence of gases such as methyl bromide, Vikane (sulfuryl fluoride), formaldehyde and phosphine, which are used as biocides to control pests or other organisms in the goods or packing materials inside the container.

These measurements are conducted on all containers that are to be inspected, regardless of whether they have a sticker indicating that they have or have not been fumigated. If one of the above gases is detected in a container, the container must be de-gassed at a separate location during hours when no people are in the immediate surroundings. A gas-free declaration is provided only after no gas can be detected in the container, and the container is then released for inspection.

The following problems have emerged from the operational method of the Rotterdam customs office, as described above.
- Not all fumigated containers that enter the country become gas-free during the trip to the Netherlands;
- Fumigated containers do not always have a sticker indicating that the container has been fumigated;
- The use of various measurement apparatus by different companies sometimes leads to different measurement results;
- The prescribed measurement strategy for making a gas-free declaration is not followed by most of the fumigation companies.

Together with the RIVM, the *Inspectie Milieuhygiëne Zuid-West* (Environmental Inspectorate for the Southwest Region) is currently designing a study to determine the magnitude of these problems. In preparation for the study, a two-day indicative measurement campaign was conducted in the Rotterdam harbour area. The results of this campaign are reported below.

2. AIM

The aim of this study was to answer the following questions:
- Of the containers that were selected for inspection, which ones contained gaseous biocides such as methyl bromide and formaldehyde?
- Did these containers have a “gas sticker”?[1]
- What were the concentrations of the biocides, if present?
- To what extent can the use of different types of measurement apparatus lead to different measurement results?

3. THE APPROACH OF THE STUDY

For this indicative study, measurements were conducted on containers that were selected for inspection by the customs office; these measurements were conducted during a two-day period by various organizations/companies using various types of apparatus. According to the specifications of the suppliers, the apparatus that were used were all suitable for the direct

[1] Gas sticker: a sticker attached to the container indicating that the container has been fumigated and specifying the fumigant used.

measurement of gas concentrations in the containers. If containers were found to contain gas (according to the measurement apparatus used), then samples were taken using an adsorption medium. A precise measurement of the gas concentration was provided by laboratory analysis of the medium. These containers were then moved to a separate location for de-gassing.

4. ORGANIZATIONS INVOLVED IN THE CAMPAIGN

The following organizations and companies were involved in the measurement campaign:
- Customs office
- IMH Zuid-West
- Kramer Container Depots
- Holland Fumigation (fumigation company)
- KLPD (*Korps Landelijke Politie Diensten* – national police service)
- Imbema (supplier of Gasmet FT-IR)
- Thermo Analytical (supplier of Miran Sapphire)
- Roteb
- Reaktie (supplier of Voyager)
- RIVM

5. APPARATUS

The following apparatus were used in this study:
- Photovac 10SPlus portable gas chromatograph (RIVM)
- SpektraTrak mobile gas chromatograph/mass spectrometer (RIVM)
- Dräger gas detection tubes (Holland Fumigation)
- Voyager portable gas chromatograph (Kramer/Reaktie)
- Gasmet Fourier-transform infrared analyzer (Imbema)
- Miran Sapphire infrared analyzer (Thermo Analytical)
- Interscan Vikane analyzer (Kramer/Reaktie)

These apparatus are briefly described in the following section.

5.1 VOYAGER PORTABLE GAS CHROMATOGRAPH

The advantages of this instrument are its portability, rapid analysis time and the fact that the analysis results can be read immediately. In principle, gases such as methyl bromide and formaldehyde can be measured both qualitatively and quantitatively. However, this is possible only under the following conditions:
1. The Voyager must be regularly calibrated, preferably immediately before the measurements and using the specific gases that will be measured;
2. The composition of the sample must be known: the Voyager "recognizes" substances based on the time it takes for them to pass through the chromatography column (retention time), but different components that pass through the column at the same rate cannot be distinguished from each other.
3. The resulting chromatograph, in combination with the numerical results provided by the Voyager, must always be interpreted by a qualified operator. The shape of the peaks nearly always provides information about how the analysis results must be interpreted.

If these conditions are not met, it is likely that the analysis results of the Voyager GC could be interpreted as a false negative or false positive.

5.2 PHOTOVAC 10SPLUS PORTABLE GAS CHROMATOGRAPH

Roughly the same limitations apply to the Photovac 10SPlus as to the Voyager GC, but with the extra limitation that the column and detector in the Photovac 10SPlus are not equally suitable for detecting both methyl bromide and formaldehyde. The chromatograms of the Photovac

10SPlus must also be interpreted by a qualified operator to avoid false-positive and false-negative results.

5.3 MIRAN SAPPHIRE

The Miran Sapphire uses infrared spectrometry.
This technology can simultaneously measure methyl bromide, Vikane, phosphine and formaldehyde in air at the ppm level. The high limit of detection is one of the disadvantages of this instrument. Because the MAC values for methyl bromide, phosphine and formaldehyde are lower than or equal to 1 ppm, which is difficult to measure with this instrument, it is unsuitable for making gas-free declarations. In practical terms, the relatively large sensor of the instrument is difficult to manoeuvre between the doors of a container.

The interpretation of infrared spectra is not always simple; specific expertise is required.

5.4 GASMET FT-IR

FT-IR (Fourier Transform-Infrared) is an infrared analysis technology. In principle, this technology is highly suitable for identifying substances in an air sample. One disadvantage of the technology – or perhaps more correctly, a limitation – is the fact that the composition of the air sample must not be too complex. Moreover, humidity can affect the performance of infrared apparatus. This also results in a relatively high limit of detection.

Theoretically, the Gasmet FT-IR is capable of measuring sulfuryl fluoride, methyl bromide, phosphine and formaldehyde. False positive measurements can occur with complex samples if the apparatus is being operated by a less experienced analyst.

5.5 SPEKTRATRAK GC/MS (GAS CHROMATOGRAPH/MASS SPECTROMETER)

With gas chromatography-mass spectrometry, the components in an air sample are first separated in a gas chromatograph, after which the separated components are analyzed sequentially by mass spectrometry. Mass spectrometry can determine the structure of the substances; in other words, it is possible to identify the components.

With the GC/MS technology, false positive measurements can be virtually ruled out. One disadvantage of this apparatus is that operator must have a background in chemistry to use the GC/MS and to interpret the results. In addition, the purchase cost of the apparatus is very high.

5.6 INTERSCAN VIKANE ANALYZER

Vikane (sulfuryl fluoride) is a biocide that is increasingly being used for fumigating containers. The only instrument that we know of for measuring this gas is the Vikane analyzer, an instrument that uses pyrolysis to convert sulphur compounds into SO_2, which is then detected by a photo-ionization detector.

In principle, this method is suitable for measuring concentrations of sulfuryl fluoride if the instrument is correctly calibrated (using a calibration gas). Nothing is known about cross-sensitivity for other substances. However, in practice (not during the present study), two Vikane analyzers have sometimes provided differing results; the cause of this discrepancy is unknown.

5.7 PH3 SENSOR

The PH3 sensor that was used in the study works with an electrochemical cell. An air pump is used to draw the air sample across the electrochemical cell. PH3 molecules defuse in the cell, and result in a voltage difference. The voltage difference is proportional to the concentration of PH3 in the sampled air. The disadvantage of this measurement principle is the cross-sensitivity of the cell to substances other than PH3. Although it is also known to what extent many frequently occurring substances interfere with the PH3-sensitive cell. Moreover, PH3 is often used for specific cargoes; as a result, it can often be determined in advance whether the presence of PH3 can be expected. However, false-negative and false-positive measurements are both possible with the PH3 sensor.

5.8 DETECTION TUBES

Detection tubes work according to the colouration principle. The substance to be detected, in this case methyl bromide, causes a colour reaction with the substance or substances in the detection tube; the intensity of the colouration is a measurement of the concentration of methyl bromide in the air that is drawn into the detection tube. The coloration is specific for methyl bromide, although there is some cross-sensitivity for chlorinated alkenes. Nevertheless, the risk of false-positive or false-negative measurements remains small. Disadvantages are that it is often difficult to read the concentration (the distinction between coloured and non-coloured may not be obvious) and the tube must be read immediately (the colouration can either increase or fade with time).

6. IMPLEMENTATION OF THE RESEARCH

The research was conducted on 26 and 27 April 2001, at the *Douanescan (*customs office scanning facility) on the Maasvlakte in Rotterdam. Gas measurements using one or more of the above instruments were conducted on all containers that were selected for inspection by the customs office.

7. MEASUREMENT STRATEGY

Initially, the gas measurement was conducted at the door opening of the container between the rubber seals of the doors, possibly with the doors opened slightly. If nothing could be measured at this location, the container was opened, and the technicians – equipped with independent respiratory protection (compressed air) – climbed inside the container to conduct another measurement.

If the presence of a biocide was detected by one of the instruments, measurements were taken with the other instruments to check if they also provided a positive indication for the relevant component. If at least one instrument yielded a positive result, an air sample was taken from the container on an adsorption medium and sent for laboratory analysis; in this way, the nature and concentration of the substance, if any, could be confirmed. This also took place when signals were obtained that could not be attributed to a known biocide. In a single case (27/4: MOAU 000486-9) a laboratory sample was collected before the fumigation company had arrived to conduct measurements.

8. SAMPLING AND LABORATORY ANALYSIS

The air samples for laboratory analysis were taken as follows:

- Methyl bromide:

Air from the container was drawn at a known flow rate (approximately 100 ml/min) through an adsorption tube filled with petroleum charcoal for a known period of time (approximately 30 minutes). The samples were taken in duplicate, using two tubes in series. Immediately after sampling, the tubes were coded and sealed and stored cold. On both 26 April and 27 April, samples were taken to the laboratory for analysis.

- Formaldehyde:

Air from the container was drawn at a known flow rate (approximately 100 ml/min) through a DNPH adsorption cartridge, specifically suitable for aldehyde adsorption, during a sampling period of approximately 30 minutes. The samples were made in duplicate, using two cartridges in series. After sampling, the tubes were sealed and stored cold. Formaldehyde sampling took place only on 27 April. That same day, the samples were shipped on ice to the laboratory.

9. RESULTS

9.1 MEASUREMENT RESULTS

Tables 1a (26 April) en 1b (27 April) show which types of apparatus were used to conduct which field measurements and the results that were obtained. The tables also show (in italics) which containers were sampled for laboratory analysis.

Table 1a: Measurement results on 26 April 2001

Container code	Gas known[2]	Instrument	Detected gas	Concentration
SCZU796200-8[3]	MeBr	Voyager	n.d.	
		SpektraTrak	n.d.	
		Photovac	n.d.	
HLCU425330-1[4]	*MeBr*	*SpektraTrak*	*MeBr and MeCl*	*Unknown*[5]
		Photovac	*Possible MeBr*[6]	*Unknown*
TRIU500566-7		Voyager	n.d.	
		SpektraTrak	n.d.	
		Photovac	n.d.	
		Interscan	n.d.	
		PH3 sensor	n.d.	
		Voyager	n.d.	
CLHU229287-6		*SpektraTrak*	*norflurane, ethanol*	*Unknown*[4]
		Photovac	*n.d.*	
		Miran	*MeBr*	*4 ppm*
		Voyager	*n.d.*	
CLHU821114-6		SpektraTrak	n.d.	
		Photovac	n.d.	

- Italics: these are the containers from which an air sample was taken for laboratory analysis.
- n.d.: nothing detected

[2]) type of gas already known due to task assignment or previous measurement
[3]) gas was previously detected in this container and it was being de-gassed at a separate location
[4]) gas was previously detected in this container and it was being de-gassed at a separate location
[5]) no calibration gas was available for the SpektraTrak
[6]) deviating peak shape in chromatogram

Table 1b: Measurement results on 27 April 2001

Container code	Gas known	Instrument	Detected gas	Concentration
SEAU223656-0[7]		SpektraTrak	Methanol, ethanol, acetone	Not determined[8]
		Voyager	n.d.	
		Interscan	n.d.	
		Photovac	n.d.	
SCZU76200-8	MeBr	SpektraTrak	n.d.	
		Photovac	MeBr (uncertain)[9]	
NOSU431848-1		SpektraTrak	Methanol, ethanol, acetone, acetic acid methyl ester, methyl formate	
		Photovac	Possible methyl bromide 9 peaks	1 ppm
INKU284214-1		*SpektraTrak*	*Methanol*	
		Photovac	*Signals of unknown substances*	
		Detection tube	n.d.	
NOSU443870		Voyager	n.d.	
		Photovac	n.d.	
		Interscan	n.d.	
MOAU000486-9		*Voyager*	*n.d.*	
		Photovac	*n.d.*	
		Miran 1B2	*No acetone or formaldehyde*	
HJCU878190-0		Photovac	MeBr	6 ppm
		Detection tube	MeBr	4 ppm
		Voyager	MeBr	2.4 ppm

- Italics: these are the containers from which an air sample was taken for laboratory analysis.
- n.d.: nothing detected

Table 2 shows the analysis results of the air in the containers in which gas was detected (not gas-free). The only container that still contained methyl bromide at a concentration higher than the MAC value of 0.25 ppm was container HLCU425330-1. No phosphine or Vikane was detected in any of the containers.

Table 2: Analysis results

Container code	Date	Adsorbent	Substance	Concentration (ppm)
CLHU229287-6	26 April	DNPH	Formaldehyde	0.07
HLCU425330-1	26 April	Active charcoal	MeBr	0.625
INKU284214-1	27 April	DNPH	Formaldehyde	n.d.
MOAU000486-9	27 April	DNPH	Formaldehyde	n.d.

- n.d.: nothing detected

[7]) gas was previously detected in this container and it was being de-gassed at a separate location (also sampled on 26 july)

[8]) no quantification was performed because these components are not biocides

[9]) deviating peak shape in the chromatogram indicated overlap with other substances: quantification not possible

9.2 OBSERVATIONS

During the measurement campaign, observations were also made of the methods of the fumigation companies. The fumigation companies always take the first measurement in between the rubber seals of the container doors. If this measurement turns out to be negative, the technician uses independent respiratory protection to enter the container. Skin protection is not used.

Measurements inside a loaded container are often difficult to conduct. The cargo, which is stacked in boxes to the ceiling of the container, often forms a wall which cannot be penetrated with a sensor or climbed. In these situations, it is very difficult to conduct a measurement to determine if the container is gas-free. According to hearsay, gas-free certificates are regularly awarded based only on measurements "at the door".

The employees of the company that conducted the measurements with the Voyager had taken a training course from the supplier of the apparatus. The course primarily focused on operating the instrument and much less on interpreting the results.

10. DISCUSSION

10.1 FIELD MEASUREMENTS

The results of the air measurements in the containers did not contradict the results of previous observations in practice: for some containers, one instrument indicated a positive result, while another instrument detected nothing.

The explanations for these differences in measurement could be based on the following differences:

- The type of instrument
  The various instruments showed varying sensitivity to the substances to be measured and to possible interfering conditions (for example humidity); moreover not all instruments were calibrated before the measurement campaign. Due to the measurement principles on which the instruments operate, false-positive or false-negative measurements are sometimes produced.
  The colouration limit of detection tubes cannot always be read unequivocally.
- Measurement location and time
  Most measurements were conducted sequentially at the door of the container. Due to ventilation through the open door, concentration differences can occur. In addition, measurements were conducted further inside the container (by means of a probe), where the concentration can also differ from the "door concentration" (due to less air circulation).

10.2 LABORATORY ANALYSIS

In addition, the gas concentrations determined by laboratory analysis (see Table 2) were different than the concentrations measured in the field. This difference could be caused by the following:

- location
  Generally speaking, the air samples for laboratory analysis were taken from the middle of the containers, in contrast with the "door measurements" taken by most of the mobile measurement apparatus.
- sampling and storage
  It is especially difficult to take samples of methyl bromide and formaldehyde: methyl bromide is very volatile and is not easily adsorbed onto media, while formaldehyde reacts

quickly with other substances. To prevent further losses, the samples were shipped on ice to the laboratory.

10.3 CALIBRATION OF MEASUREMENT APPARATUS

The fumigation company that uses the Voyager apparatus to make gas-free declarations has the instrument calibrated to the substances to be measured once per month. However, we believe that a gas chromatograph should be calibrated at least before every measurement campaign. During calibration, not only the concentration of the target substances is checked, but also the shape of the chromatograms. As a result, a possible shift in the peaks or contamination of the column can be ascertained.

Because the chromatograms are not examined as part of the operational method of the Voyager operators, false-positive measurements can occur. Indeed, the company has experienced false-positive measurements several times in practice. False-negative measurements are also conceivable, but have not yet been observed.

For that matter, all measurement apparatus (with the exception of the detection tubes and the PH_3 sensor) require calibration with a calibration gas before taking quantitative measurements.

10.4 GAS-FREE CERTIFICATES

If there is truth in the assertions of third parties that containers are declared gas-free based only on measurements taken between the rubber seals of the container doors, then it is possible that some containers could be incorrectly declared gas-free. When measuring at the doors, where there is a relatively large amount of ventilation, there is a risk of that a zero value could be measured even though the cargo within the container is still saturated with gas.

10.5 VOYAGER USER TRAINING PROGRAMME

We have the impression that the user training programme for the Voyager does not sufficiently address the gas chromatography background of this instrument. The training programme primarily addresses the operation of the apparatus, even though a good interpretation of the results of gas chromatography is at least as important, and is generally more difficult than simply pressing the correct buttons to conduct a measurement.

10.6 TRAINING PROGRAMMES FOR USING THE OTHER APPARATUS

With the exception of the detection tubes and the PH_3 sensor, the apparatus used in this study should be operated by a chemical analyst or someone with comparable expertise and experience; this is especially important for the correct interpretation of the measurement results. Even the use of detection tubes and the PH_3 sensor requires experience, for example to predict where there is a risk of interference in specific situations.

10.7 PERSONAL PROTECTION AIDS

In view of the operational methods of the fumigation companies during the two measurement days, it should be noted that the use of skin protection is recommended. After all, some components – certainly methyl bromide – can also be absorbed through the skin.

11. CONCLUSIONS

Of the 10 containers selected for inspection, two turned out to contain methyl bromide in a concentration above the MAC value for this substance. Only one of these containers had a sticker indicating that the container had been fumigated.

With the exception of the mobile gas chromatograph/mass spectrometer, in this indicative study no instruments were used with which an unknown biocide in a container could be identified at a level which is at or below the MAC value for the corresponding substances.

In principle (at the ppm level) it is also possible to identify substances with FT-IR, but mixtures of substances are often difficult to interpret; consequently this instrument is also unusable for identifying the composition of the air in a container. We must conclude that a universal, easy-to-operate instrument for identifying substances in the air inside possibly fumigated containers and for providing gas-free certification does not yet exist.

Based on the four most widely used biocides, this means that containers which may have been fumigated must be subjected to a series of specific measurements for a sequence of components. Apparatus that are relatively resistant to interference and are relatively simple to use are the following:

- detection tubes: for methyl bromide, formaldehyde and phosphine,
- Interscan: for sulfuryl fluoride (Vikane),
- PH3 sensor for phosphine.

Quantitative measurements of a specific component can be conducted only after the gas with which the container has been fumigated has already been identified; the quantitative measurement can then be conducted with a gas chromatograph (calibrated before the measurement at the ppb level), an FT-IR or an infrared spectrophotometer (both calibrated at the ppm level).