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Determination of phosphine and other fumigants in air samples by thermal desorption and 2D heart-cutting gas chromatography with synchronous SIM/Scan mass spectrometry and flame photometric detection

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ABSTRACT

Fumigants and volatile industrial chemicals are particularly hazardous to health when a freight container is fumigated or the contaminated material is introduced into its enclosed environment. Phosphine is now increasingly used as a fumigant, after bromomethane – the former fumigant of choice – has been banned by the Montreal Protocol. We have enhanced our previously established thermal desorption–gas chromatography–mass spectrometry (TD-GC–MS) method by integrating a second gas chromatographic dimension and a flame photometric detector to allow the simultaneous detection of phosphine and volatile organic compounds (VOCs), providing a novel application. A thermal desorption system is coupled to a two dimensional gas chromatograph using both mass spectrometric and flame photometric detection (TD-2D–GC–MS/FPD). Additionally, the collection of mass spectrometric SIM and Scan data has been synchronised, so only a single analysis is now sufficient for qualitative scanning of the whole sample and for sensitive quantification. Though detection limits for the herewith described method are slightly higher than in the previous method, they are in the low $\mu L\,m^{-3}$ range, which is not only below the respective occupational exposure and intervention limits but also allows the detection of residual contamination after ventilation. The method was developed for the separation and identification of 44 volatile substances. For 12 of these compounds (bromomethane, iodomethane, dichloromethane, 1,2-dichlorethane, benzene, tetrachloromethane, 1,2-dichloropropane, toluene, trichloronitromethane, ethyl benzene, phosphine, carbon disulfide) the method was validated as we chose the target compounds due to their relevance in freight container handling.

1. Introduction

Fumigation is a method of pest control in the course of which buildings or containers are completely filled with gaseous pesticides or fumigants such as phosphine to suffocate or poison the pests within. In particular, it is used during processing of goods to be imported or exported to prevent transfer of exotic organisms. In order to circumvent personal injury, thorough aeration has to take place and air samples from the inside of closed fumigated rooms or containers have to be analysed prior to allowing personnel access for control or discharge purposes. Fumigation for the quarantine and phytosanitary treatment of cargo, storehouses and mills is regulated by the United Nations Food and Agricultural Organisation (UN FAO), although the implementation, compliance and monitoring varies considerably throughout the world [1,2].

Current methods for routine monitoring of residual fumigants in treated areas are usually too specific or not sensitive enough to detect hazardous substances at and below their recommended exposure levels [1]. Consequently, many incidents of accidental exposure have left persons affected and gravely ill for the rest of their lives. Another problem is the wide variety of substances that may be present [2,3], which include not only fumigation agents but also many industrial chemicals that permeate the goods and their packaging [1,2]. The increasing adoption of novel, more effective and cheaper fumigants for application means that a detection strategy must be suitable for sensitive screening as well as for the detection of specific target analytes.

Bromomethane has been the insecticide of choice, but is being phased out after the Montreal Protocol recognized its strong ozone

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depletion properties and increasingly phosphine is chosen as a replacement [3–5].

Phosphine is a popular insecticide for the fumigation of food, tobacco, and natural products during shipment in freight containers or bulk carriers and during storage in ware houses and mills [3,6,7]. Now, phosphine is also increasingly used as a post-harvest application for dried figs, post-harvest and quarantine treatment of almonds, and post-harvest disinfection of citrus fruits [8–10], although insect resistance is expected to limit its efficiency in future [3,7]. The antifungal properties of phosphine have also been investigated and discussed [11,12] making phosphine an even more attractive fumigant for transported commodities.

Only a few techniques for the sampling and analysis of airborne phosphine have been discussed in the recent literature, namely: reactive sorption on silver nitrate impregnated tubes with subsequent elution followed by ICP-AES (inductively coupled plasma atomic emission spectrometry) analysis [13], cryo focussing with subsequent GC–ICP–MS (gas chromatography with inductively coupled plasma mass spectrometry) analysis [14], GC-NPD (gas chromatography with nitrogen phosphorus detector) analysis [15], SIFT-MS (Single Ion Flow Tube Mass Spectrometry) determination [16] or GC-TSD (gas chromatography thermionic specific detection) analysis [17], direct injection with packed column gas chromatography with alkali flame ionisation detection [18] or Real-Time Monitoring with Electrochemical Detectors interfaced by Radio Telemetry [19]. The unequivocal disadvantage of these methods is that they confine the analysis to phosphine only (or sometimes additional hydrides) and they restrict the applications to situations where the presence of phosphine is already known. Since phosphine is increasingly used as fumigant for freight containers, but its use is hardly ever declared [1,2], a more comprehensive method is needed that allows the simultaneous analysis and detection of any potential volatile contaminant. However, due to poor sensitivity for phosphine in mass selective detection, which is the best choice for the analysis of VOCs and screening for novel fumigants and other volatile contaminants, a need for a new method, sufficiently sensitive for both, VOCs and phosphine, has emerged.

The two-dimensional, heart-cutting gas chromatography described in this work provides a practical solution. Initial separation of VOCs from each other and from phosphine takes place on the first dimension column. The phosphine peak is then transferred to the second dimension column which elutes to a flame photometric detector in phosphorus mode. A wide variety of volatile substances can be screened by mass spectrometric detection, while phosphine can be sensitively analysed by specific flame photometric detection.

Thermal desorption coupled to GC–MS is often used for the analysis of air samples [20–22]. The samples are either collected by active sampling on sorbent tubes and analysed by dual stage desorption (by desorption from the tube and refocusing on a cold trap and final desorption from the cold trap to the GC column) or the samples are collected in canisters or Tedlar bags and the analytes are directly focussed on the cold trap. Cold traps may be cryogenically or electronically cooled by a Peltier element. In the current study, we employed Tedlar bag sampling, where the analytes were directly focussed on an electronically cooled trap.

Conventional GC–MS analytics uses the Scan mode for scanning the sample extracts for expected and unexpected substances as a qualitative analysis while the SIM mode yields good sensitivity for quantitative analysis of the target compounds. Newer instruments, like the Agilent 5975 Mass Spectrometer Series, reduce the time-consuming effort by consolidating the collection of SIM and Scan into a single measurement step. Careful parameter setting ensures an imperceptible loss in chromatographic and spectral quality [23,24].

In the present work, a method to detect phosphine along with VOCs in container air samples using a thermal desorption system coupled to a two dimensional gas chromatograph with mass spectrometric and flame photometric detection (TD-2D–GC–MS/FPD) is presented. By incorporating simultaneous collection of SIM and Scan data, a single analysis is sufficient for qualitative screening and quantitation of all target compounds. We have applied the method to a set of 53 freight container air samples for the measurement of phosphine in a complex mixture of various unknown VOCs.

2. Experimental

2.1. Reagents, supplies and equipment

A certified test mixture of 39 compounds, each about 100 $\mu L\,m^{-3}$,[1] in the gas phase was purchased from Scott (Scott Specialty Gasses, PA, USA). Additionally, certified standard gases of bromomethane, phosphine and sulfuryl fluoride, 50 $mL\,m^{-3}$ each, were obtained from Linde (Linde AG, Gases Division Germany, Pullach, Germany).

Analytical grade liquid compounds, benzene, carbon disulfide, 1,2-dichloroethane, 1,2-dichloropropane, dichloromethane, ethyl benzene, iodomethane, toluene, tetrachloromethane and trichloronitromethane, were purchased from Fluka Analytical (Fluka Analytical/Sigma–Aldrich Switzerland, Buchs, Switzerland).

Three different sorbent focusing traps with varying sorbent fillings in appropriate quartz glass tubes (0.012 m length, 2.9 mm outer diameter, 1 mm internal diameter at the inlet/outlet end and 2 mm internal diameter at the other end) were evaluated: graphitised carbon black, carbon molecular sieve (U-T15ATA); graphitised carbon black, silica gel (U-T14H2S); porous polymer, graphitised carbon black, molecular sieve (U-T5O3F), and were supplied by Markes International (Markes International, Llantrisant, UK). A Vacu-Case™ vacuum pump was used for taking sample volumes of 1 L in Tedlar® air sampling bags (both Analyt MTC, Müllheim, Germany).

2.2. Instrumentation

A Markes (Markes International Limited, Llantrisant, UK) thermal desorption system was used. The system consists of a sampling device (Markes MCS06 Air server multichannel sampler) and a thermal desorber (Markes UNITY thermal desorber), connected to a 6890N gas chromatographic system (Agilent, Santa Clara, CA, USA) via a transfer line (consisting of uncoated fused silica placed in an isolated and heated sheath), connected to the GC column by a glass press fitting.

A *Deans* switch, incorporated within the GC System, allows heart-cutting two dimensional applications. For this purpose, two different detectors were attached to the GC: a 5975 mass spectrometer and a 6850 flame photometric detector (both Agilent, Santa Clara, CA, USA). The effluent from the first column, a 30 m × 0.25 mm HP-1MS column with 1 μm coating (Agilent, Santa Clara, CA, USA), which is connected to the injecting transfer line, was either sent to the MS via a restrictor tubing of deactivated fused silica or to a second column, a 25 m × 0.32 mm Varian (Paolo Alto, CA, USA) PoraPLOT Q column, which elutes to the FPD.

[1] Conversion factors from $\mu L\,m^{-3}$ ($mL\,m^{-3}$) to $\mu g\,m^{-3}$ ($mg\,m^{-3}$) for the target compounds at 23 °C (laboratory temperature): Phosphine: 1.4, dichloromethane: 3.50, bromomethane: 3.91, carbon disulfide: 3.13, 1,2-dichloroethane: 4.07, 1,2-dichloropropane: 4.65, toluene: 3.79, benzene: 3.21, ethyl benzene: 4.37, trichloronitromethane: 6.76, tetrachloromethane: 6.33, iodomethane: 5.84.

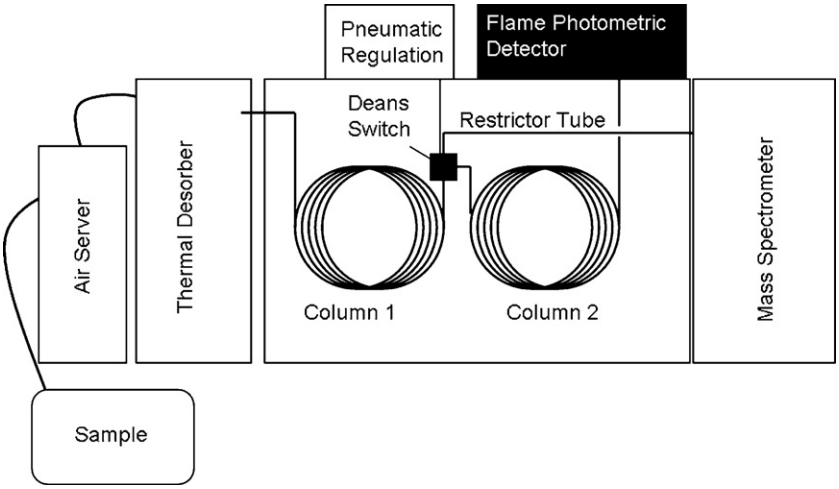

Fig. 1. Scheme of the TD-2D-GC–MS/FPD system.

2.3. Procedures

2.3.1. Sample collection

Air samples were taken via a tubular steel lance pushed through the container door seal and a silicon tube connected to a Tedlar® sample bag in the Vacu-Case vacuum pump. 1 L of air was taken from each of 53 containers arriving at the Customs Office Waltershof in the port of Hamburg.

2.3.2. Preparation of standards

Initially, a predilution was prepared by filling a 1 L Tedlar bag with 1 L of nitrogen 5.0 (Linde AG, Munich, Germany) and then injecting the appropriate volume of liquid to provide about 1000 mL m^{-3} of each component in the sample bag. The predilution was allowed to equilibrate for 1 h at room temperature. For the final standard samples, Tedlar bags were filled with 1 L of synthetic air and then an appropriate amount of the predilution, as well as phosphine standard gas and bromomethane standard gas, were added using gastight syringes. Subsequently, these standard samples were allowed to equilibrate for 1 h before the first measurement.

2.3.3. Thermal desorption

Sample bags containing standards or container air samples were directly connected to the Airserver via a teflon tube. The cold trap was electronically cooled by a Peltier element. Prior to sampling, all pathways from the sample bag to the cold trap, but excluding the cold trap itself, were flooded with sample or standard in a prepurge step. After the pre-purging, the sample was allowed to pass through the cold trap at a defined time and flow rate in order to trap a defined sample volume. The appropriate sample volume was determined as described below.

After the trapping step, all pathways and the cold trap were flushed with the gas helium 5.0 (Air Liquide, Düsseldorf, Germany) to eliminate sample from the pathways and to purge excessive oxygen from the cold trap. During this time, the trap was held at its low temperature. The gas stream from the trap during the purging procedure was conducted to a vent and did not enter the analytical GC column. Subsequently, the trap was quickly heated to the established maximum temperature of 290 °C and a stream of carrier gas in the reverse direction was used to flush the cold trap and transfer the sample via a transfer line to the analytical GC column. The transfer line temperature was kept at high temperature to prevent any deposition of analytes. The general settings for the thermal desorption unit were tested using the U-T15ATA cold trap and a standard gas of 150 μL m^{-3} phosphine, 100 μL m^{-3} of benzene and 100 μL m^{-3} dichloromethane. Each parameter (sample volume, prepurge volume, trap purge volume and flow, sampling flow, flow path temperature, trap low temperature, trap high temperature, split flow) was varied separately to obtain the best conditions. Sample volume is a very critical parameter. Care must be taken to prevent analyte breakthrough, i.e., to prevent analytes being swept through the entire sorbent bed and thus being lost from the system during the sampling process. All three cold traps were tested with different volumes (2.5, 5, 7.5, 10, 12.5, and 15 mL) of the same gas standard at a sampling flow rate of 5 mL/min to determine the breakthrough volume for each compound.

2.3.4. GC–MS/FPD analysis

The gas chromatograph was run in constant pressure mode using the *Deans* column switch. Helium 5.0 was used as carrier gas and was further purified using a Helium gas filter (Supelcarb HC, Supelco/Sigmal-Aldrich Switzerland, Buchs, Switzerland) to trap oxygen, water and hydrocarbons. The pressures set for the inlet and switching valve were calculated from the column lengths and diameters, the initial temperature of the oven program and the desired initial column flows, using the Agilent "Deans Switch Calculator". In addition, the length of the restrictor tubing from the *Deans* switch to the first detector was calculated. Fig. 1 shows the 2D-GC system schematically.

Columns were chosen to separate phosphine and sulfuryl fluoride from the VOCs on the first column and to separate phosphine from sulfuryl fluoride on the second one. Flows were set to an initial value of 3 mL/min on the first and 4 mL/min on the second column and restrictor tube, respectively. The oven temperature program was optimized to provide the best separation for the mixture of 44 compounds including 12 target compounds we considered relevant in freight container handling. An excessive number of compounds were used for the optimization of the temperature programme to consider the appearance of substances other than the target compounds. In freight container air samples the appearance of additional substances is quite usual, due to the individual scents of the transported goods.

Phosphine and sulfuryl fluoride were the first compounds of interest to elute from column 1. The corresponding peak was switched to the second column where the two compounds were separated and eluted to the FPD in phosphorus mode. All other compounds eluting from the first column were analysed by MS in Scan mode for compound identification and in selected ion monitoring (SIM) mode for quantitative determination. For this purpose, a synchronous SIM/Scan method was set up optimizing the param-

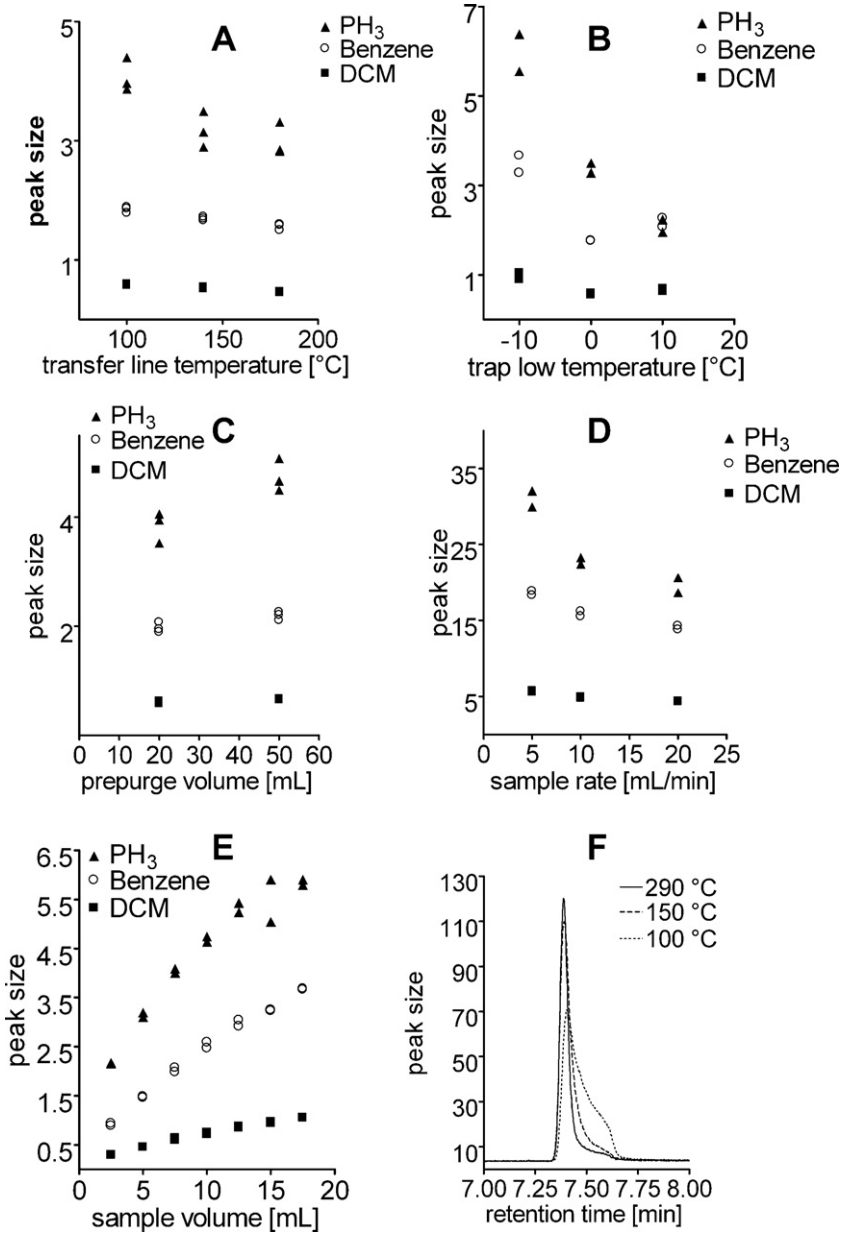

Fig. 2. Influence of different thermal desorption parameters on peak size for phosphine (PH_3, 150 μL m^{-3}), benzene (100 μL m^{-3}) and dichloromethane (DCM, 100 μL m^{-3}) (A–E). Influence of trap heating temperature on the peak shape for phosphine (F); note the different scales for the peak size.

eters as recommended [23,24]. The samples in Scan mode were set to $n = 3$. The groups in SIM were limited to 2 or 4 ions and the dwell times were set to 100 ms per ion.

2.3.5. Validation

Calibration was performed using the standard samples we prepared from liquids and standard gases with recovery determined by analysis of certified test gases, when available. For phosphine, recovery was checked by simultaneous analysis of a standard sample with a *Honeywell SPM* phosphine monitor (MDA Scientific SPM, Honeywell Analytics Distribution Inc, Lincolnshire, IL, USA). Limits of detection and quantification were derived from low concentration standard curves by appropriate equations:

$$\mathrm{LOD} = s_{x_0} \cdot t_{f,\alpha} \cdot \sqrt{\frac{1}{N_a} + \frac{1}{N_c} + \frac{\bar{x}^2}{Q_x}}$$

$$\mathrm{LOQ} = k \cdot s_{x_0} \cdot t_{f,\alpha} \cdot \sqrt{\frac{1}{N_a} + \frac{1}{N_c} + \frac{(k \cdot LOD - \bar{x})^2}{Q_x}}$$

LOD = limit of detection; LOQ = limit of quantification; s_{x_0} = standard deviation; $t_{f,\alpha}$ = factor of t distribution; N_a = number of measurements; N_c = number of calibration points; $\bar{x}$ = mean of concentrations; Q_x = sum m of square deviations; x = concentration.

2.3.6. Analysis of freight container air samples

To test the method for its applicability to real-world samples, it was applied to 53 freight container air samples taken at the Customs Office Waltershof in the port of Hamburg in September 2009. Containers were chosen either randomly or according to estimates of contamination obtained by onsite devices (GDA II, Airsense Analytics, Schwerin, Germany and Voice 200, Syft Technologies, Christchurch, New Zealand) or after considering the probability of

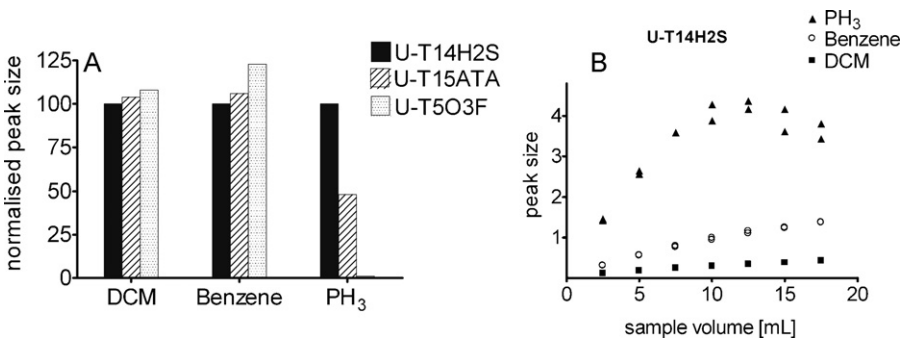

Fig. 3. (A) Comparison of three different cold traps for benzene (100 μL m^{-3}), dichloromethane (DCM, 100 μL m^{-3}) and phosphine (PH3, 150 μL m^{-3}); (B) Determination of breakthrough volume for the U-T14H2S cold trap.

fumigation with phosphine. Some samples had to be reanalysed after dilution when the detected concentration exceeded the linear range of calibration.

3. Results and discussion

3.1. Sample collection

The collection of samples in Tedlar bags is often discussed because of concerns about substances being adsorbed by the bag material or being lost by diffusion during storage [25–28]. These contentious points were addressed in a series of storage experiments (data not shown). Tedlar bags show the advantage that they are easier to handle and to transport than canisters. The samples were always analysed within 24 h after sampling and the Tedlar bags were not reused.

Sorbent tubes could not be considered for use because a very volatile substance like phosphine is not sufficiently retained at ambient temperature.

3.2. Thermal desorption

The effects of the most critical parameter settings, tested with the U-T15ATA cold trap, are shown in Fig. 2. By lowering the trap high temperatures during desorption from the trap, greater peak areas were obtained but they resulted in distorted peak shapes for phosphine (Fig. 2F). Comparisons determined that the U-T14H2S trap was best suited for the cold trapping of benzene, dichloromethane and phosphine. Although the peak sizes for benzene and dichloromethane were slightly greater with the other cold traps, phosphine was trapped 50 and 100 times more effectively by the U-T14H2S trap (Fig. 3A). The derived parameters are listed in Table 1.

3.3. Gas chromatographic separation

As demonstrated in Fig. 4 using the adapted GC programme settings (Table 1), a mixture of 42 volatile organic substances was well separated in the first dimension on the HP-1MS column (Fig. 4A), while phosphine and sulfuryl fluoride were separated sufficiently in the second dimension on the PLOT column (Fig. 4B).

The use of a flame photometric detector in phosphorus mode for detecting the effluent from the PLOT column leads to a high detection limit for sulfuryl fluoride (5 mL m^{-3}). Thus, a second run with only MS detection was necessary to measure this compound. In future, we intend to test the splitting of the effluent from the second column with the integration of an electron capture detector (ECD) as a third detector.

3.4. Synchronous SIM/Scan analysis

As peak widths at the base are about 6 s and the scanned mass range is 203 m/z wide, the settings for scan sampling rate (n = 3) and ion dwell time (100 ms/ion) result in about 9–12 SIM/Scan cycles per peak, which is in good agreement with recommended acquisition rates for SIM and Scan analysis [29]. In comparison, the SIM only method with the same SIM parameters results in 15 (4 ions/group) or 30 (2 ions/group) scans per peak and a comparable Scan method (n = 4) results in 11.5 scans per peak. Thus, the selected settings for synchronous SIM/Scan analysis resulted in no significant decline of peak integrity, sensitivity or spectral quality (Fig. 5). By combining the screening feature of TIC and the sensitivity of SIM analysis, the use of synchronous SIM/Scan analysis results in a considerable time saving and the assignment of peaks from the SIM chromatogram is corroborated by the simultaneous recording of full mass spectra.

Table 2 shows the main target compounds, their retention times and their quantifier and qualifier ions. These compounds were chosen due to the frequency of their detection in the atmospheres of freight containers [2]. These substances were integrated in the SIM

Table 1
Optimized instrumental parameters.

TD-parameters	
Prepurge	10 min, 5 mL/min
Sampling	1 min at 5 mL/min
Trap low temperature	−10 °C
Trap high temperature	290 °C
Trap high interval	4;min
Split flow during trap desorption	5 mL/min
Transfer line temperature	108 °C
GC-parameters	
Inlet pressure (constant)	0.347 MPa
Valve pressure (constant)	0.275 MPa
Initial flow rates column 1, column 2	3 mL/min, 4 mL/min
Carrier gas	He 5.0
Temperature program	35 °C hold 4 min, 9 °C/min to 70 °C, hold 5 min, 8 °C/min to 200 °C, 25 °C/min to 240 °C, hold 4 min
Switch to column 2	min 2–2.6
MS-parameters	
EI conditioning	70 eV
Mass range	47–250 amu
Threshold	150 counts
MS quad temperature	200 °C
MS source temperature	250 °C
Scan rate	n = 3
Ion dwell time in SIM	100 ms
SIM group size	2 or 4 ions
FPD-parameters	
Filter	P-filter
Temperature	250 °C
Air	100 mL/min
Hydrogen	75 mL/min

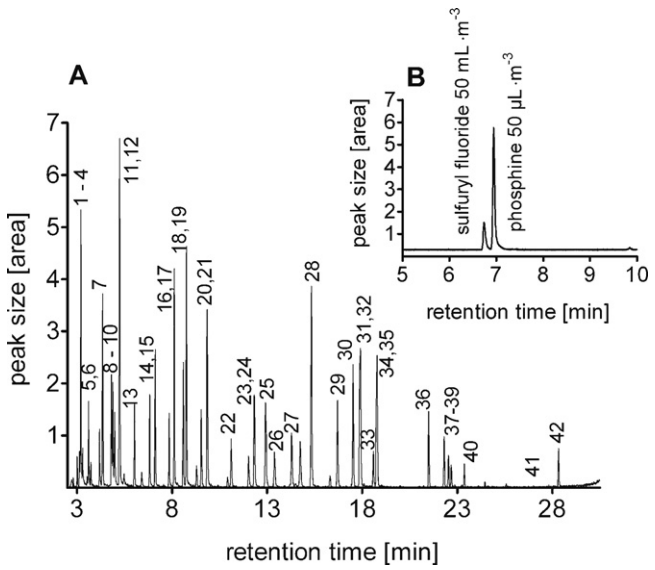

Fig. 4. (A) Chromatogram of 42 VOCs in the first dimension; (B) sulfuryl fluoride and phosphine in the second dimension. 1: Dichlorodifluoromethane; 2: Chloromethane; 3: 1,2-Dichloro-1,1,2,2-tetrafluoroethane; 4: Chlororethene; 5: Bromomethane; 6: Chloroethane; 7: Trichlorofluoromethane; 8: Iodomethane; 9: 1,1-Dichloroethene; 10: Dichloromethane;11: 1,1,2-Trichloro-1,2,2-trifluoroethane; 12: Carbon disulfide; 13: 1,1-Dichloroethane; 14: *cis*-1,2-Dichloroethene; 15: Trichloromethane; 16: 1,2-Dichloroethane; 17: 1,1,1-Trichloroethane; 18: Benzene; 19: Tetrachloromethane; 20: 1,2-Dichloropropane; 21: Trichloroethene; 22: *cis*-1,3-Dichloro-1-propene; 23: *trans*-1,3-Dichloro-1-propene; 24: 1,1,2-Trichloroethane; 25: Toluene; 26: Trichloronitromethane, 27: 1,2-Dibromoethane; 28: Tetrachloroethene; 29: Chlorobenzene; 30: Ethylbenzene; 31, 32: *m*- and *p*-Xylene; 33: Styrene; 34, 35: 1,1,2,2-Tetrachloroethane and *o*-Xylene; 36: 1,3,5-Trimethylbenzene; 37: 1,2,4-Trimethylbenzene; 38: 1,3-Dichlorobenzene; 39: 1,4-Dichlorobenzene; 40: 1,2-Dichlorobenzene; 41: 1,2,4-Trichlorobenzene; 42: Hexachloro-1,3-butadiene.

groups and a calibration was performed for quantitative analysis. Other substances were analysed in TIC mode only and quantified from a one point calibration (data not shown).

3.5. Validation

The method validation results are also listed in Table 2. Standard curves showed very good linearity in the range from 2 to 400 $\mu L\,m^{-3}$ for phosphine ($R^2 = 0.999$) and from the limit of quantification to about 1100 $\mu L\,m^{-3}$ for the other substances ($R^2 = 0.994–1.000$).

Recovery ranged between 93% and 100% at 98–110 $\mu L\,m^{-3}$ for all tested analytes except for bromomethane, which was found at only 87% of the certified concentration. At 283 $\mu L\,m^{-3}$ of phosphine and 1000–1050 $\mu L\,m^{-3}$ of the other target substances the recovery was between 98% and 106% except for ethyl benzene, which was found with 138% of recovery.

Limits of detection ranged between 1 and 4 $\mu L\,m^{-3}$, limits of quantification between 2 and 12 $\mu L\,m^{-3}$. This was not as low as LODs and LOQs reported for ambient air analysis by other groups using thermal desorption with tubes [30,31] with their greater preconcentration, while direct focussing on the cold trap is much more limited by breakthrough volume. Nevertheless, these values are more than adequate as they are well below the recommended exposure limits defined for Germany [32]. By calculating from the signal to noise ratio, lower LODs would be obtained (between 0.1 and 3 $\mu L\,m^{-3}$), but the authors regard the calculation from low level standard curves to be more reliable. The relative standard deviation between 1% and 5% at 100 $\mu L\,m^{-3}$ and between 1% and 3% at 1000 $\mu L\,m^{-3}$ for all substances except phosphine. At 50 and 300 $\mu L\,m^{-3}$ of phosphine the relative standard deviation of this compound was 3%.

3.6. Analysis of freight container air samples

Concentrations of 12 target analytes investigated in 53 containers are summarized in Table 3. A severe decline in the linear range for phosphine was observed during the course of the investigation. This was probably due to the cold trap being exposed to high concentrations and this problem was resolved by reconditioning the cold trap at 320 °C while purging with carrier gas.

Table 3 reveals that phosphine was only found in containers transporting dry bulk foodstuffs, such as rice, spices or nuts. 9 out of 53 investigated containers were contaminated with phosphine at concentrations from 36 to 6899 $\mu L\,m^{-3}$. In Germany, the recommended limit value for discharging phosphine-treated units is 10 $\mu L\,m^{-3}$ [32]. The atmospheres in these contaminated containers were additionally compromised by other substances, presumably from previous loads transported in the same container. However, the relatively high levels of toluene, benzene and 1,2-dichloroethane in sample 17 are indicative of pollution by the current load.

None of the containers analysed was contaminated with sulfuryl fluoride which was analysed by a one dimensional TD-GC–MS method described previously [2]. As sulfuryl fluoride is registered as a trade fumigant, we will try to upgrade the described method by splitting the effluent from the second column and integrating a third detector. A second run for sulfuryl fluoride will then be dispensable.

Dichloromethane, 1,2-dichloroethane, benzene, toluene, ethyl benzene, and carbon disulfide were most frequent and also exhibited the highest maximum concentrations. The levels of dichloromethane, 1,2-dichloroethane, benzene, toluene and ethyl benzene were significantly higher than those recently found in

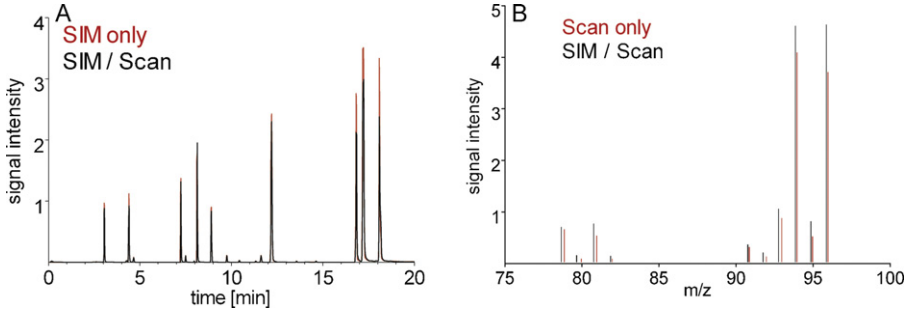

Fig. 5. (A) Comparison of SIM chromatograms of 9 compounds (bromomethane, dichloromethane, 1,2-dichloroethane, tetrachloromethane, 1,2-dichloropropane, toluene, ethyl benzene, *m*- and *p*-xylene, *o*-xylene). (B) Mass spectra of bromomethane in Scan mode and combined SIM/Scan mode.

Table 2
Quantifier and qualifier ions and validation results of the target analytes.

Compound	Monitored ions in MS [m/z]	t_R [min]	LOD [$\mu L\,m^{-3}$]	LOQ [$\mu L\,m^{-3}$]	Linear range [$\mu L\,m^{-3}$]	R^2	RSD [%][a]	RSD [%][b]	Recovery			
									Test gas [$\mu L\,m^{-3}$]	Recovery [%]	Test gas [$\mu L\,m^{-3}$]	Recovery [%]
Phosphine	–	6.5	1	2	2–400	0.999	3	3	98[c]	100[c]	269[c]	98
Dichloromethane	48.9 (100); 83.9 (94)	4.6	2	7	7–1064	1.000	2	2	110	100	1040	101
Bromomethane	94 (100); 78.8 (12)	3.2	3	9	9–1101	0.999	2	3	100	87	1040	105
Carbon disulfide	75.9 (100)	4.9	2	5	5–1081	1.000	2	2	–[d]	–[d]	–[d]	–[d]
1,2-Dichloroethane	62 (100); 48.9 (21); 98 (5)	7.5	1	3	3–1089	1.000	1	1	110	99	1040	106
1,2-Dichloropropane	62.9 (100); 76 (56); 48.9 (17.6)	9.2	3	7	7–1073	0.999	1	2	110	96	1040	106
Toluene	91 (100); 65.1 (10); 51 (6)	12.6	2	6	6–1085	1.000	1	2	110	95	1030	113
Benzene	78 (100); 51 (15); 63 (4)	8.2	2	6	6–1089	0.999	2	2	110	93	1040	105
Ethyl benzene	91 (100); 105.9 (29); 50.9 (12)	17.2	3	11	11–1070	0.999	3	5	110	97	1050	138
Trichloronitromethane	118.9 (100); 116.8 (95); 81.9 (30)	13.1	4	12	12–1105	0.994	5	3	–[d]	–[d]	–[d]	–[d]
Tetrachloromethane	116.9 (100); 81.9 (28)	8.4	2	5	5–1080	0.998	2	2	110	99	1000	103
Iodomethane	141.9 (100); 126.8 (40)	4.4	2	6	6–1091	1.000	1	2	–[d]	–[d]	–[d]	–[d]

t_R = retention time, RSD = relative standard deviation, LOD = limit of detection, LOQ = limit of quantification.

[a] 3 Replicates of a 100 $\mu L\,m^{-3}$ (50 $\mu L\,m^{-3}$) standard sample of each compound (phosphine).

[b] 3 Replicates of a 1000 $\mu L\,m^{-3}$ (300 $\mu L\,m^{-3}$) standard sample of each compound (phosphine).

[c] Agreement with phosphine online device.

[d] No test gas available.

Table 3
Results of the field campaign during september 2009.

Container number	Concentration of target analytes in $\mu L\,m^{-3}$ and the container cargo at the time of sampling												
	Bromomethane	Iodomethane	Dichloromethane	1,2-Dichloroethane	Benzene	Tetrachloromethane	1,2-Dichloropropane	Toluene	Trichloronitromethane	Ethylbenzene	Phosphine	Carbon disulfide	Cargo
1	<LOD	<LOD	<LOQ	11	19	<LOD	<LOD	16	<LOD	16	<LOD	22	Textiles
2	<LOD	<LOD	<LOD	<LOQ	228	<LOD	<LOD	994	<LOD	138	<LOD	57	Chem. products
3	<LOD	<LOD	<LOQ	24	122	<LOQ	<LOD	456	<LOD	65	<LOD	7	Textiles
4	<LOD	<LOD	<LOD	<LOQ	62	<LOD	<LOD	238	<LOD	40	<LOD	7	Shoes
5	<LOD	<LOD	<LOQ	3	37	<LOD	9	143	<LOD	30	<LOD	<LOQ	Textiles
6	<LOD	<LOD	<LOQ	5	20	<LOD	<LOD	130	<LOD	44	<LOD	6	Constr. material
7	<LOD	<LOD	5102	3	8	<LOD	<LOD	79	<LOD	19	<LOD	10	Furnishings
8	<LOD	<LOD	<LOQ	5	9	<LOD	11	484	<LOD	17	<LOD	117	Furnishings
9	<LOD	<LOD	5758	92	30	<LOQ	<LOD	776	<LOD	16	<LOD	23	Furnishings
10	<LOD	<LOD	15	13	119	<LOD	<LOD	1110	<LOD	50	<LOD	17	Vehicles/parts
11	<LOD	<LOD	<LOD	<LOQ	10	<LOD	<LOD	184	<LOD	54	<LOD	<LOQ	Constr. material
12	<LOD	<LOD	65	10	32	<LOD	<LOQ	282	<LOD	3807	<LOD	13	Furnishings
13	<LOD	<LOD	<LOQ	654	104	<LOD	107	846	<LOD	1751	<LOD	13	Furnishings
14	<LOD	<LOD	13	35	29	9	10	333	<LOD	47	<LOD	<LOQ	Natural product
15	9	<LOD	<LOQ	17	15	<LOQ	<LOQ	194	<LOD	35	<LOD	5	Foodstuff
16	<LOD	<LOD	9	194	101	<LOD	<LOD	2268	<LOD	47	<LOD	76	Shoes
17	<LOD	<LOD	<LOQ	316	2630	<LOQ	<LOD	4240	<LOD	31	36	12	Bulk foodstuff
18	<LOD	<LOD	8	206	1569	<LOQ	<LOD	2382	<LOD	55	<LOD	8	Textiles
19	<LOD	<LOD	12	33	48	<LOD	16	2415	<LOD	24	<LOD	47	Textiles
20	<LOD	<LOD	<LOD	4	22	<LOD	<LOD	181	<LOD	20	<LOD	<LOQ	Furnishings
21	<LOD	<LOD	<LOD	3	27	<LOQ	<LOD	47	<LOD	12	<LOD	<LOQ	Furnishings
22	<LOD	<LOD	<LOD	6	22	<LOD	<LOD	53	<LOD	14	<LOD	<LOD	Vehicles/parts
23	<LOD	<LOD	67	36	35	<LOD	<LOD	15,379	<LOD	512	<LOD	17	Furnishings
24	<LOD	<LOD	<LOD	9	50	<LOD	<LOD	752	<LOD	24	<LOD	<LOQ	Vehicles/parts
25	<LOD	<LOD	<LOD	47	50	<LOD	<LOD	785	<LOD	25	<LOD	<LOQ	Natural product
26	96	<LOD	<LOD	5	14	<LOQ	<LOQ	136	31	14	<LOD	<LOD	Natural product
27	<LOD	<LOD	<LOD	<LOQ	11	<LOD	<LOD	225	<LOD	<LOQ	676	<LOD	Bulk foodstuff
28	<LOD	<LOD	<LOD	4	12	<LOD	<LOD	128	<LOD	13	<LOD	<LOD	Bulk foodstuff
29	<LOD	<LOD	<LOQ	<LOQ	<LOQ	<LOD	<LOD	78	<LOD	52	<LOD	<LOQ	Furnishings
30	<LOD	<LOD	14	114	61	<LOD	<LOD	1101	<LOD	26	<LOD	<LOD	Foodstuff
31	<LOD	<LOD	8	42	25	<LOD	<LOD	588	<LOD	<LOQ	<LOD	6	Furnishings
32	<LOD	<LOD	9	29	32	<LOD	<LOD	1434	<LOD	107	<LOD	<LOD	Shoes
33	<LOD	<LOD	<LOD	5	15	<LOD	<LOD	112	<LOD	<LOD	<LOD	<LOD	Foodstuff
34	<LOD	<LOD	<LOD	<LOD	8	<LOD	<LOD	85	<LOD	<LOD	<LOD	<LOD	Textiles
35	<LOD	<LOD	9	9	24	<LOD	12	81	<LOD	19	<LOD	9	Furnishings
36	<LOD	<LOD	<LOD	5	15	<LOD	9	225	<LOD	42	<LOD	6	Bulk foodstuff
37	<LOD	<LOD	76	12	76	<LOD	<LOQ	8654	12	10,557	<LOD	6	Electr. devices
38	<LOD	<LOD	9	53	50	15	30	171	<LOD	136	6899	14	Bulk foodstuff
39	<LOD	<LOD	<LOD	<LOQ	<LOQ	<LOD	<LOD	49	<LOD	16	<LOQ	<LOD	Bulk foodstuff
40	<LOD	<LOD	1	<LOD	<LOQ	<LOD	<LOD	336	<LOD	14	<LOD	<LOQ	Textiles
41	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	534	<LOD	23	<LOD	<LOD	Textiles
42	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	66	<LOD	<LOD	<LOD	<LOD	Constr. material
43	<LOD	<LOD	86	3254	118	<LOD	17,143	47,071	<LOD	122	<LOD	<LOD	Shoes
44	<LOD	<LOD	130	6809	265	<LOD	38,123	270,310	<LOD	213	<LOD	<LOD	Shoes
45	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	602	<LOD	<LOD	327	<LOD	Bulk foodstuff
46	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	1199,5	<LOD	<LOD	3363	<LOD	Bulk foodstuff
47	<LOQ	7	<LOQ	6	<LOQ	<LOD	3	57	<LOD	46	210	<LOQ	Bulk foodstuff
48	<LOD	5	<LOQ	<LOQ	<LOQ	<LOD	1	20	<LOQ	<LOD	<LOD	<LOQ	Bulk foodstuff
49	<LOQ	<LOQ	<LOQ	21	18	<LOD	3	198	<LOD	28	167	<LOQ	Bulk foodstuff
50	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	31	<LOD	<LOD	440	<LOD	Bulk foodstuff
51	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	57	<LOD	<LOD	386	<LOD	Foodstuff
52	<LOD	<LOD	13	221	90	<LOD	607	10,286	<LOD	126	<LOD	<LOQ	Shoes
53	<LOD	<LOD	<LOQ	8	6	<LOD	<LOQ	57,401	<LOD	95	<LOD	19	Shoes

LOD = limit of detection; LOQ = limit of quantification.

urban and industrial air in Tarragona, Spain, by Ras et al. and for benzene, toluene, and ethyl benzene in residential and commercial urban areas in Rio de Janeiro, Brazil, by Martins et al. [20,30,33]. For benzene and ethyl benzene, the minimum observed concentrations in this study (6 $\mu L\,m^{-3}$ (19.3 $\mu g\,m^{-3}$) benzene and 12 $\mu L\,m^{-3}$ (52.4 $\mu g\,m^{-3}$) ethyl benzene) were equal to or higher than maximum levels reported by these studies (6.6–27.9 $\mu g\,m^{-3}$ benzene and 11.2–65.5 $\mu g\,m^{-3}$ ethyl benzene, respectively).

Iodomethane was not found in any of the samples, though its use as a fumigant was already reported [34,35] and after the ban of bromomethane might be used in container fumigation as a replacement.

Trichloronitromethane, better known as chloropicrin, was an additive to bromomethane for fumigation to generate a warning smell. During the study we found chloropicrin in two samples. But only one was associated with the finding of bromomethane (Container number 26). In the other case chloropicrin was related to high concentrations of ethyl benzene and toluene. This might be an example of an undefined mixture of substances used as pesticides. For bromomethane and iodomethane chloropicrin was found to increase their efficacy as fumigants [34].

Bromomethane was found in two samples throughout this study, which comprises 4% of the investigated containers and suits our findings of declining bromomethane use in freight container fumigation [2]. In neither of the two cases, the German limit value for unloading containers of 500 $\mu L\,m^{-3}$ [32] was exceeded.

Phosphine was found in 9 of the 53 investigated freight containers. In all cases the German limit value for unloading freight containers of 10 $\mu L\,m^{-3}$ [32] was exceeded. Only in half of the cases the containers were signed with a warning label indicating high phosphine concentrations.

Carbon disulfide was found in 43% of the investigated samples. The concentrations were moderate between 5 and 117 $\mu L\,m^{-3}$ and none of the samples exceeded the occupational exposure limit for carbon disulfide, which is 5 $mL\,m^{-3}$ in the European Union and 1 $mL\,m^{-3}$ in the United States. Tetrachloromethane was only found in two freight containers at minor concentrations of 9 and 15 $\mu L\,m^{-3}$.

1,2-Dichloropropane was found in 26% of the investigated containers. In three cases the concentrations were noticeably high (38,123, 17,143, and 600 $\mu L\,m^{-3}$). All of these containers were transporting shoes, which might indicate the use of this compound as a chemical used in production of shoes or treatment of leather. 1,2-Dichloropropane is known to be part of dry cleaners, used in paint manufacturing and in insecticidal fumigant mixtures [36], but information on its use in production processes is lacking.

4. Conclusions

The current method was established and validated for the investigation of air samples for the detection of fumigants and industrial chemicals residues. The synchronous SIM/Scan feature provides advantages in time saving and reliability, while the heart-cutting feature and synchronous flame photometric detection enables the simultaneous detection of phosphine, the most important and frequently applied fumigant of foodstuffs and recently for container fumigation.

The detection of sulfuryl fluoride by FPD in phosphorus mode has shown to be only possible at concentrations exceeding 5 $mL\,m^{-3}$. Because phosphine and sulfuryl fluoride cannot be separated in the first dimension, a second run is still necessary to analyse samples for sulfuryl fluoride by MS with a detection limit of 2 $\mu L\,m^{-3}$. We will try to solve this shortcoming by integrating a third detector.

The low limits of detection and quantification of phosphine and VOCs are important for the frequent case of multiple contaminations and the resulting risk of synergistic detrimental effects on human beings as well as possible exposures of highly susceptible subjects such as unborn children, those with cardio respiratory or other serious disorders.

In the field, the method has proven to be practicable and it can now be applied to a greater set of samples in future studies. For severely contaminated samples with excessively high concentrations, a modified method with a lower sample volume or higher split flow during analysis will be established to circumvent time-consuming and error-prone dilution steps.

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