GERSTEL Application Note No. **197**, *2018*

Automated Determination of Formaldehyde Emissions from Materials by On-Sorbent Derivatization and Thermal Desorption GC/MS

Yunyun Nie, Lokman Coban, Shuai Li, and Eike Kleine-Benne

GERSTEL GmbH & Co. KG, Eberhard-Gerstel-Platz 1, 45473 Mülheim an der Ruhr, Germany

KEYWORDS

Pentafluorophenylhydrazine (PFPH), Tenax-TA, Dynamic Headspace (DHS), GC/MS, plywood, candle, formaldehyde, carbonyl compounds

ABSTRACT

A new fully automated thermal desorption (TD)-GC/MS method was developed for determination of formaldehyde and other airborne carbonyls as well as VOCs for material emission testing. The method includes an automated in-situ derivatization agent loading step prior to every sampling step, thus blank values are avoided. Pentafluorophenylhydrazine (PFPH) was used as derivatization agent and was automatically loaded onto Tenax TA adsorbent using a dynamic headspace (DHS) technique. Repeat use of Tenax TA adsorbent for loading PFPH and the background of PFPH-CH_2O was validated, the usefulness of Tenax TA adsorbent for the analysis, as well as the storage behavior of PFPH loaded Tubes were investigated. The linearity of the formaldehyde calibration curve from 0.2 - 2.0 µg (corresponding to 8 - 81 nmol) for the PFPH/TD-GC/MS method was r^2 = 0.9989 with average RSDs of only 1.4% (4 levels, n=5). The method provided good reproducibility. The limit of detection (LOD) for formaldehyde was calculated according to DIN 32645 to be 0.09 µg (3.0 nmol) and the limit of Quantitation (LOQ) was determined to be 0.25 µg (8.33 nmol). Emissions from a plywood sample and a commercially available candle were analyzed using the PFPH/TD-GC/MS method. Formaldehyde and the VOCs and SVOCs normally determined by Tenax/TD-GC/MS were all determined. Formaldehyde was detected in both sample types.

INTRODUCTION

The standard technique used for determination of formaldehyde and other carbonyl compound emissions from building materials in indoor air and/or test chamber air (ISO 16000-3, ASTM D5197-09, AgBB) is to draw a sample through a 2,4-dinitrophenyl hydrazine (DNPH) coated cartridge/tube followed by solvent elution with acetonitrile and analysis of a small fraction of the derivatives/eluent using high-pressure liquid chromatography (HPLC) combined with UV detection. This technique has been used for more than 3 decades [1], but there is widespread interest in improving or replacing it with a combined method for a wider range of VOCs including those normally determined by TD-GC/MS.

DNPH cartridges/tubes are consumable items, which are not inexpensive. After sampling they must be stored at temperatures below 4°C [2], adding cost and complicating overall handling. Since the standard technique relies on liquid elution, less than 0.5 % of the DNPH derivatives formed are normally transferred to the HPLC system, resulting in high method detection limits. Additionally the separation power of HPLC is limited, especially for similar carbonyls (e.g. acetone, acrolein and propanal) [1]. Furthermore, the DNPH sorbent is suitable for formaldehyde, acetaldehyde and acetone, but not for hexanal and higher aldehydes/ketones due to their slower derivatization reaction resulting in significant analyte discrimination when compared to results from TD/GC-MS methods based on Tenax TA sorbent use [2,3]; Last, but not least the hydrozones collected on DNPH-coated cartridges have been observed to undergo transformation into several unknown compounds (derivatives). This means that, for example, acrolein cannot be determined using standard methods (ASTM D 5197, ISO 16000-3). In previous work, we have overcome this problem by including the sampling process in the method calibration. Meanwhile, there has been a huge increase in demand for acrolein analysis over the past decade due to the introduction of the Chinese Standard HJ/T 400-2007 [4] .

In summary, DNPH/HPLC is limited to determining formaldehyde and acetaldehyde, and not suitable for the determination of acrolein, hexanal and aldehydes and ketones higher than C_4.

The reaction of DNPH and PFPH are shown separately (Figure 1). The five fluorine atoms in PFPH make this hydrozone more thermally stable and more volatile than the hydrozone derivatives of DNPH. The feasibility of PFPH TD-GC/MS approach has been demonstrated by Cecinato et al. [5] in 2001 and the advantages of PFPH as a derivatization agent over O-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBHA) have been demonstrated by Ho et al. [1].

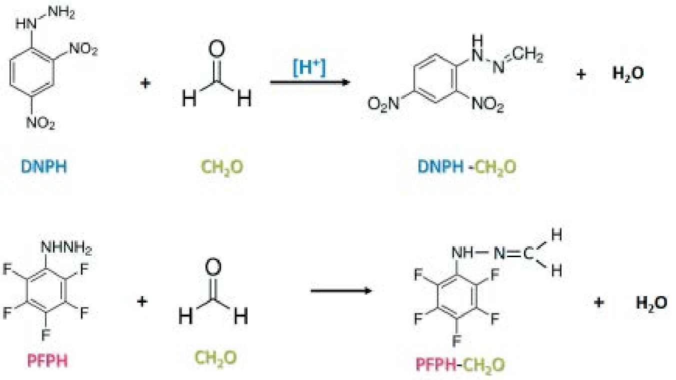

Figure 1. Reaction of DNPH and PFPH with formaldehyde.

In 2004, Ho et. al published a new approach for the determination of formaldehyde and other airborne carbonyls using on-sorbent derivatization based on pentafluorophenylhydrazine (PFPH) and TD-GC/MS. Using this PFPH/GC method, carbonyls in gaseous samples were successfully determined, including formaldehyde, acetaldehyde, propanal, butanal, heptanal, octanal, acrolein, 2-furfural, benzaldehyde, p-tolualdehyde, glyoxal and methylglyoxal. The method was shown to deliver high collection efficiency, good linearity and method detection limits (MDLs) of sub-nanomoles per sampling tube [1].

In our view, the only drawback of the PFPH derivatization TD-GC/MS method developed by Ho et al. [1] is the manual step of packing the tube with PFPH loaded Tenax TA. Following thermal desorption, the Tenax TA sorbent must be removed for recoating with PFPH and the tube repacked. Manual loading of the tubes increases the risk of high blank values because the derivatization reagent is exposed to ambient air. If handling of the derivatization reagent and sampling is combined in one automated device with a limited and constant time period between the steps, the blank value problems can be solved and the inconvenience of manual handling eliminated. In the work presented here, such an in-situ loading and sampling system is presented. An automated PFPH/GC method was developed that includes loading PFPH onto the TenaxTA tube, sampling onto the PFPH loaded Tenax TA, thermal desorption, and GC-MS analysis (see Figure 2). In the work reported here we focused on formaldehyde, even though several gaseous carbonyl compounds have been successfully determined using the same method [1]. A further goal was to optimize the method for reusability of the Tenax TA sorbent after thermal desorption and to limit carryover and background signal. Further the formaldehyde loading capacity of Tenax TA was determined in addition to the optimal sampling rate of gaseous formaldehyde with regard to the kinetics of the reaction with PFPH coated Tenax TA. Validation data was generated, based on formaldehyde calibration standards, the linearity and repeatability of the method were determined. Finally, the method was used to determine formaldehyde emission from two sample types: Plywood and a candle. In a separate AppNote, we report on the determination of formaldehyde in e-cigarette liquids using the same analysis method.

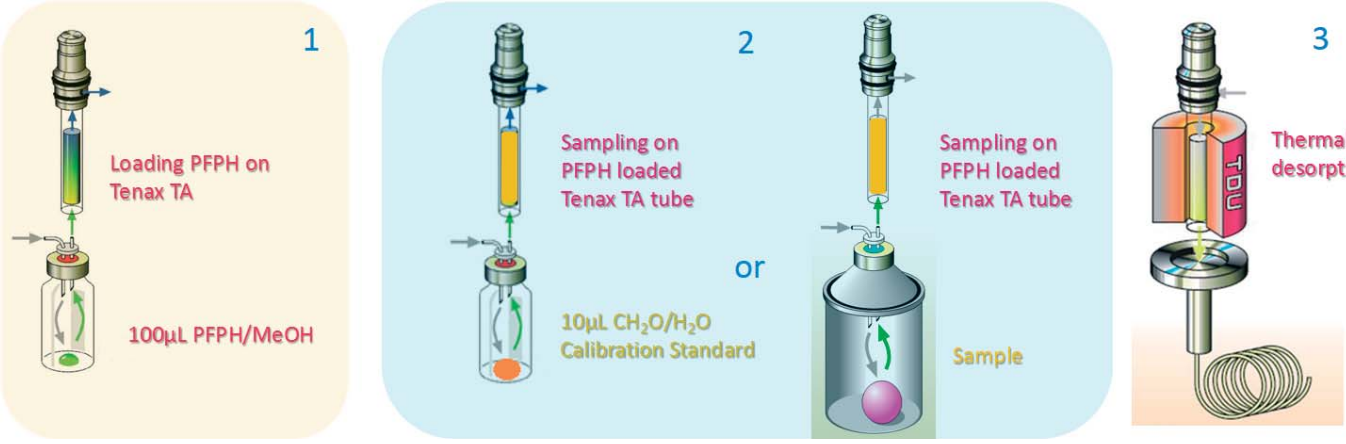

Figure 2. Schematic drawing of the PFPH/TD-GC/MS method steps.

A dynamic headspace technique (Dynamic Headspace (DHS), GERSTEL) was used for automated loading of PFPH onto the Tenax TA tube as well as for sampling gaseous formaldehydes and other volatile and semi-volatile organic compounds (VOCs and SVOCs) from the sample. A purge gas such as, for example, helium, nitrogen, or synthetic air is continuously introduced into a sealed sample container, in which the sample has been placed, and analytes are swept from the sample headspace onto an adsorbent tube positioned at the outlet. For this project nitrogen was used. In DHS analysis, analytes are extracted more efficiently compared with static headspace and are concentrated on the adsorbent tube. In this study, Tenax® TA sorbent was chosen since it can trap and release both VOCs and SVOCs and has very low affinity to water. Depending on the sample size, the sample container used can be varied from 4 mL to 1000 mL- if the analysis system is configured with a DHS Large sampler.

Following the DHS step, the sorbent tube is transferred to the thermal desorption unit (TDU 2, GERSTEL) and the analytes thermally desorbed and subsequently cryofocused in the Cooled Injection System (CIS 6, GERSTEL) cold trap. The CIS 6 is finally heated using a temperature program and the analytes introduced to the GC/MS system as a narrow band leading to improved peak shape and separation as well as increased sensitivity. The complete DHS-TD-GC/MS analysis is automated using the GERSTEL MultiPurpose Sampler (MPS), the complete system is shown in Figure 3.

Figure 3. Automated DHS/ DHS large-TD-GC/MS system used in this work.

Experimental

Materials. Pentafluorophenylhydrazine PFPH (97 %, Sigma Aldrich), methanol (≥ 99,9 %, ROTH), formaldehyde (37 wt. % in H_2O, containing 10-15 % Methanol as stabilizer, Sigma Aldrich), HPLC Water (Promochem®). A PFPH stock solution was prepared by dilution with methanol under a nitrogen atmosphere reaching a concentration of 1.44 mM. Formaldehyde calibration solutions were prepared by spiking different volumes of formaldehyde stock solution into water to obtain five levels: 0.02, 0.04, 0.12, 0.24, and 0.4 µg/µL.

A plywood sample, a wooden base plate of a box containing wooden building blocks for children 1 year and older was purchased online. The 6 cm x 9 cm sample was cut out of the base plate and both sides were exposed during sampling. Candles with apple and pear scent in green color (Size: 14 cm x 7 cm OD) were purchased at a local store.

Analysis Conditions
DHS:

Incubation Temp.:	30°C (for PFPH loading), 50°C (formaldehyde calibration)
Purge Gas:	Nitrogen
Purge Volume:	700 mL (PFPH Loading), 500 mL (formaldehyde calibration)
Purge Flow:	50 mL/min (PFPH loading), 40 mL/min (formaldehyde calibration)
Trap Temp.:	20°C
TDU:	30°C, 720°C/min, 280°C (1 min)
CIS/PTV:	20°C, 15°C/min, 280 °C (2 min); Tenax TA liner; split 1/40
Carrier Gas:	Helium
GC Column:	HP-5 (50 m x 320 µm x 0.52 µm)
Oven Program A:	40°C (1 min), 25°C/min, 154°C, 15°C/min, 280°C (2 min) (used for calibration based on PFPH and PFPH-CH_2O standards)
Oven Program B:	40°C (2 min), 10°C/min, 280°C (2 min) (used for samples)
MSD:	Scan, 30-450 amu

DHS and CIS parameters used for determination of formaldehyde emissions from plywood and a candle:

Sample	Analytes	DHS				CIS/PTV (Tenax TA Liner)	
		Sorbent Tube	Purge Volume [mL]	Purge Flow [mL/min]	Incubation Temp. [°C]	Initial Temp. [°C]	Split ratio
Plywood	VOCs	Tenax TA	1000	50	Room temp.	-30	1:10
	CH_2O + VOCs	PFPH + Tenax TA	500	40	Room temp.	-30	1:40
Candle	VOCs	Tenax TA	1000	50	Room temp.	-30	1:40
	CH_2O + VOCs	PFPH + Tenax TA	1000	40	Room temp.	-30	1:40

RESULTS AND DISCUSSION

Manual loading of PFPH and its drawbacks. At the beginning, manual injection of PFPH stock solution into Tenax TA tube was tried. After injection of 200 µL PFPH stock solution (the maximum loading capacity for 2 cm Tenax TA bed), the Tenax TA tube was put in the fume hood over night to dry. This approach resulted in significantly higher PFPH-formaldehyde background values after 1 day (69 %), 2 days (92 %) and 10 days (215 %) storage respectively of the PFPH loaded Tenax TA tubes in the fume hood. Direct injection of 1 µL PFPH stock into PTV (CIS 6) did not result in a PFPH-CH_2O peak (Figure 5), which indicates that the formation of PFPH-CH_2O is mainly due to uptake of formaldehyde from laboratory air.

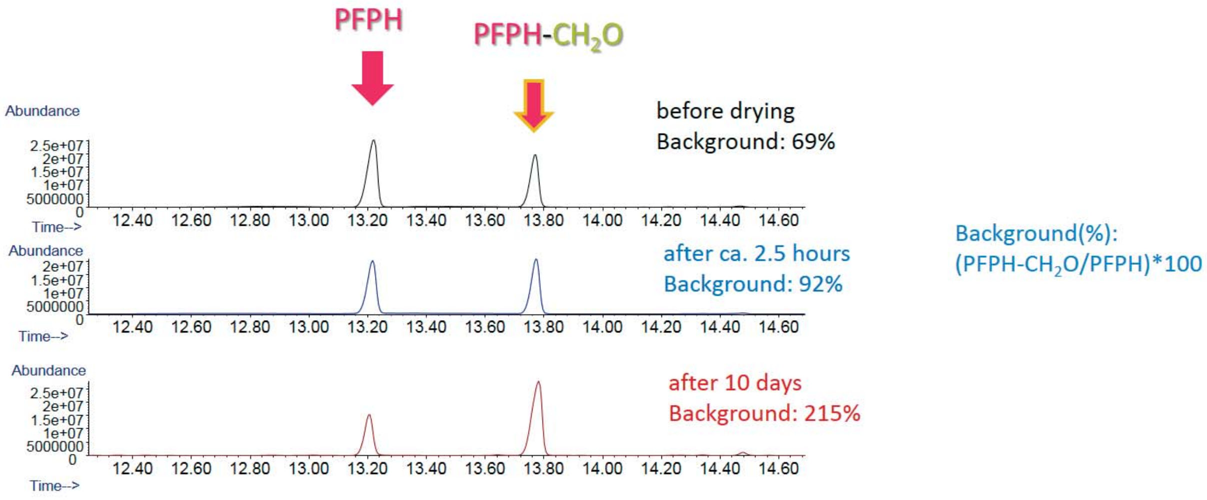

Figure 4. Chromatograms obtained after different drying periods for PFPH-loaded tubes placed in a fume hood.

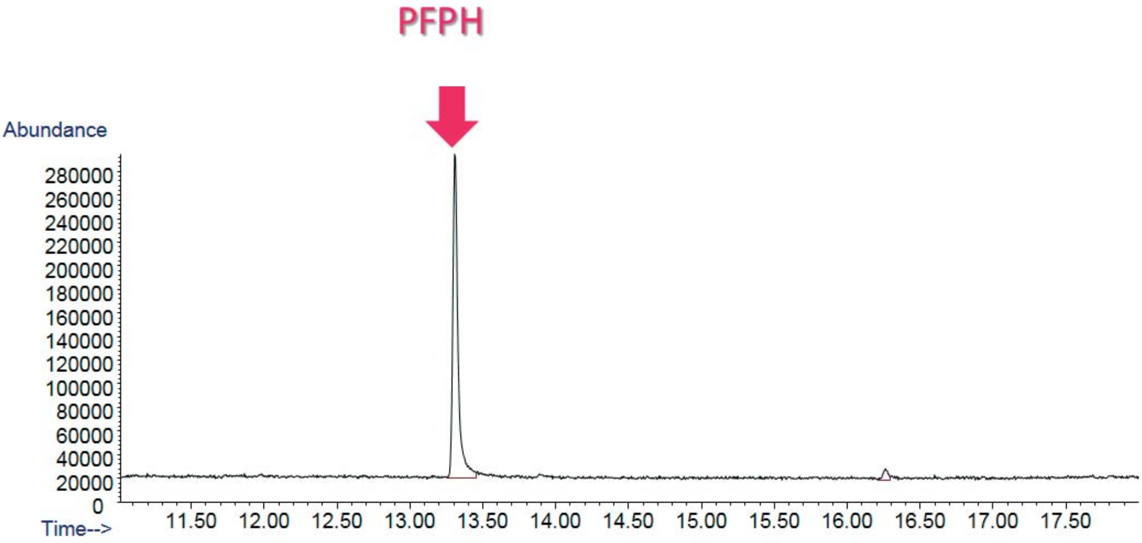

Figure 5. Chromatogram resulting from injection of 1 µL PFPH stock solution directly into the CIS/PTV inlet.

Loading Tenax-TA tubes with PFPH using dynamic headspace - Minimizing the PFPH-CH_2O background. To eliminate contact with air during PFPH loading and drying on Tenax TA filled tubes, an automated dynamic headspace (DHS) approach was evaluated, which relies on a completely sealed system. PFPH stock was placed in a 2 mL closed small vial in the sample tray on the MultiPurpose Sampler (MPS). To load a Tenax TA tube, the required amount of PFPH was transferred from the vial to a sealed 10 mL headspace vial. The vial was subsequently transported to the DHS sample position, where incubation and/or sampling is performed. A double-needle is part of the standard system and it is used to pierce the septa of the 10 mL headspace vial: Through one needle, inert gas is purged into the vial. Through the other, the gaseous PFPH in the headspace is removed from the vial headspace and directly trapped on the Tenax TA tube. Since methanol is not retained on Tenax TA, it was used as solvent to generate the standards used.

By using DHS for PFPH loading, the PFPH-CH_2O contamination peak was reduced dramatically to the range of 0.6 – 2.5 % (Figure 6). Five repeat loadings of 100 µL PFPH on five different Tenax TA tubes resulted in good reproducibility with RSDs of only 4.3 %. A PFPH-loaded Tenax TA tube can be reused after undergoing a thermal desorption step (280°C for 1 minute). A second run directly after PFPH desorption showed no carryover as can be seen in Figure 7.

In 100 µL PFPH stock solution, the total amount of PFPH was calculated to be 144 nMol. The sample incubation temperature used was 30°C, purge flow rate 50 mL/min, and purge volume ≥ 700 mL for a complete PFPH transformation. The Tenax TA adsorbent was kept at 20°C. Under these conditions, the PFPH in the sample vial was shown to be quantitatively transferred into Tenax TA tube. A second run directly thereafter using the same vial and DHS-TDU method resulted in a clean background (no PFPH or PFPH-CH_2O was detected), which indicates that the derivatization agent was quantitatively transferred to the tube.

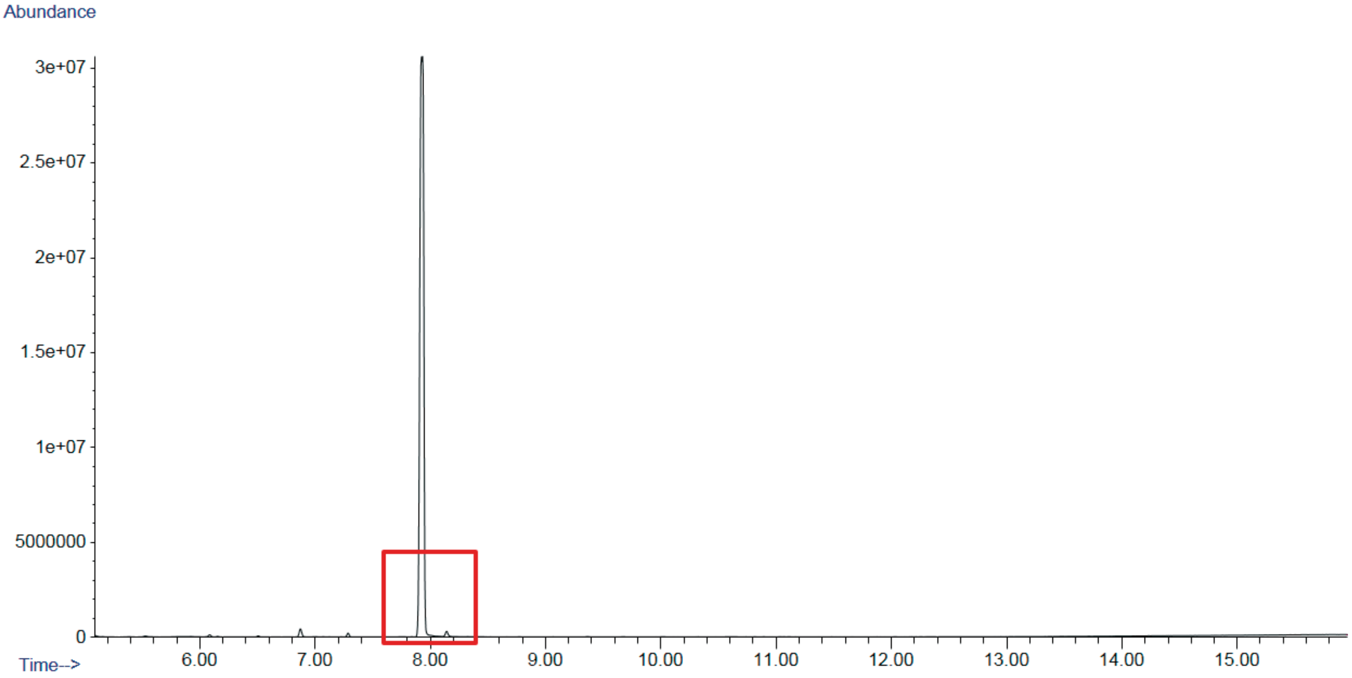

Figure 6. Peaks of PFPH and PFPH-formaldehyde after DHS loading of 100 µL PFPH stock solution and split 1/40.

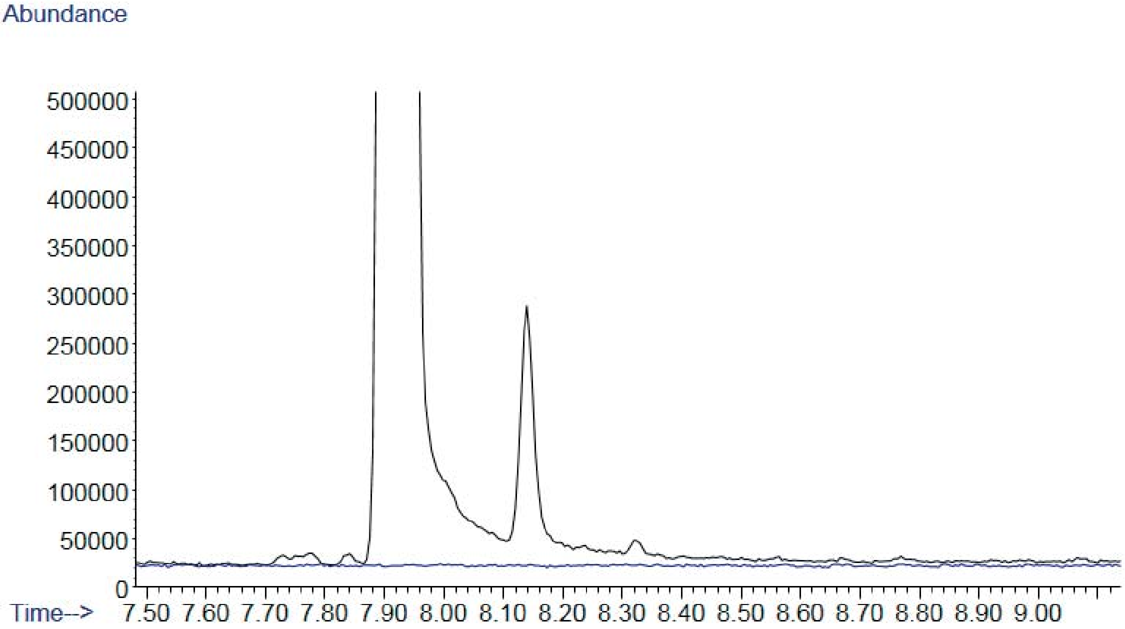

Figure 7. Comparison of a chromatogram obtained from thermal desorption of a Tenax TA tube loaded with 100 µL PFPH and a background chromatogram of the same Tenax TA tube desorbed directly afterwards (blue chromatogram).

Storage of PFPH loaded Tenax TA tubes. Six Tenax TA tubes, freshly loaded with PFPH, were stored in a TDU tray and desorbed after storage times from 0 hours (directly after loading) to 168 hours (7 days). As can be seen in Figure 8, the percentage of PFPH-CH_2O background increased with increasing storage time, from 0.6 % till 4.7 %. Still the peak was quite small even after storage for a week in the tray, indicating good long term stability of PFPH-loaded Tenax TA tubes in the autosampler. Equally it shows that it is possible to prepare PFPH tubes in the laboratory before sampling. On-site PFPH loading is therefore not needed, but feasibility of storage in transport boxes and transportation of such pre-loaded tubes was not tested in this work.

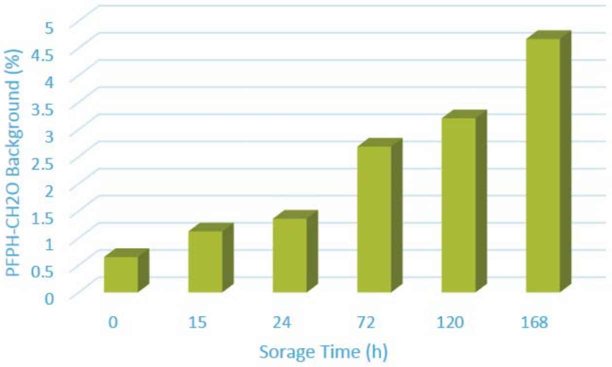

Figure 8. Stability test for PFPH loaded Tenax TA tubes stored in the TDU tray.

Sampling formaldehyde on PFPH loaded Tenax TA tubes - Collection efficiency. In the formaldehyde sampling step, a 10 μL aliquot of a formaldehyde solution was injected into a sealed 10 mL headspace vial and a freshly PFPH-loaded Tenax TA tube was used for collection. Three parameters needed to be optimized: incubation temperature, flow rate, and sampling volume for 10μL CH_2O/H_2O solution.

For formaldehyde spiked in water, an incubation temperature of higher than 50°C was found to be necessary the in order to ensure complete evaporation of the 10 μL water volume.

The most critical parameter was the flow rate. Ho et al. [1] found that the collection efficiency of carbonyls dropped as the flow rate increased from 54 mL/min to 102 ml/min and to 224 ml/min. The drop was more pronounced for the smaller carbonyls. This was explained to be caused by kinetic limitations in the reaction of formaldehyde with PFPH on the Tenax TA Tube [1]. Our experiments showed similar results. We sampled the vapor phase formed after injecting 10 μL aliquots of a formaldehyde solution into individual headspace vials using the same sampling volume and incubation temperature at flow rates ranging from 5 ml/min to 55 ml/min. As can be seen in Figure 9, at flow rates higher than 45 ml/min, the resulting PFPH-CH_2O peak area dropped significantly. A flow rate of 40 mL/min was chosen for subsequent testing.

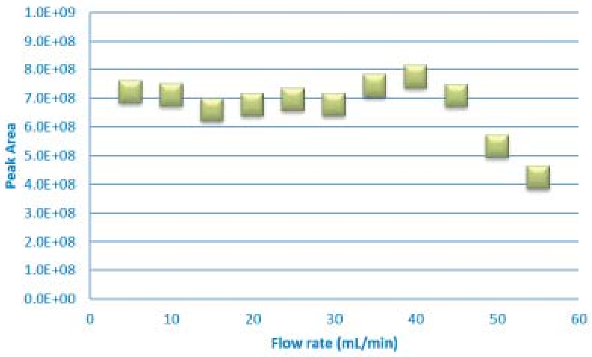

Figure 9. Flow rate optimization for sampling of 10μL formaldehyde/H_2O solution out of a 10 mL vial.

At the chosen flow rate of 40 mL/min, the minimum sampling volume for complete transfer of formaldehyde onto the PFPH loaded Tenax TA tube was determined (see Figure 10). The minimum required purge volume was found to be 350 mL nitrogen for a 10 μL CH_2O/H_2O sample. A 500 mL volume was chosen for subsequent testing.

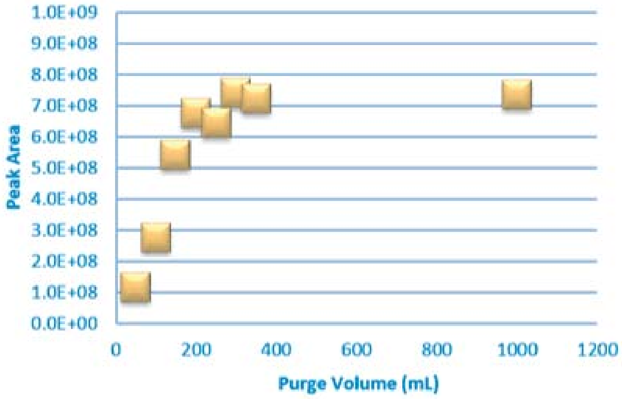

Figure 10. Purge volume optimization for 10μL formaldehyde/H_2O solution in a 10 mL vial.

Calibration of formaldehyde: Linearity, LOD and LOQ. Aqueous formaldehyde calibration solutions were prepared at five concentration levels ranging from 0.02 to 0.4 µg/µL. 10 µL aliquots of the individual solutions were injected into separate sealed 10 mL headspace vials for calibration using PFPH loaded Tenax TA tubes. The total amount of PFPH on the absorbent in each tube was 144 nmol. Formaldehyde calibration levels were calculated to range from 8 to 162 nmol. At each level, five replicates were performed. As can be seen in Figure 11, the linearity range was found to be 0.2 – 2.0 µg (corresponding to 8 - 81 nmol) with R^2=0.9989. Good reproducibility with average RSDs of only 1.4 % (4 levels, n=5) was achieved. It was found that the highest level of 162 nmol CH_2O fell outside the linear range presumably due to collection efficiency limitations. Similar results were obtained by Ho et al. who concluded that sampling with an amount of PFPH a factor of 1.8 times higher than the amount of total carbonyls provides adequate recovery of the carbonyls [1]. In our results, the linearity range reaches to an amount of 81 nmol (formaldehyde) with a calculated PFPH to formaldehyde ratio of 1.78, which correlates well with the values given by Ho et. al. The limit of detection (LOD) was calculated to be 0.09 µg (3.0 nmol) according to DIN 32645 and LOQ was calculated to be 0.25 µg (8.33 nmol).

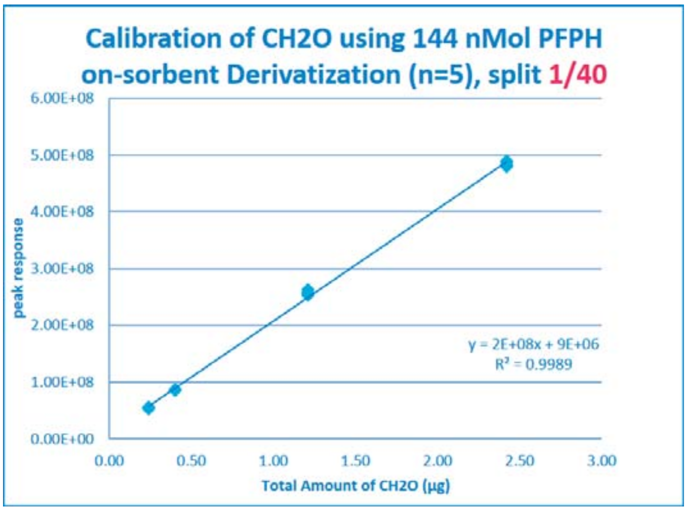

Figure 11. Formaldehyde calibration curve linearity (4 levels, n=5 each).

PFPH load optimization. PFPH loading depends not just on the amount adsorbed on Tenax TA, but also on the amount of PFPH-CH_2O formed. The percentage of PFPH-CH_2O formed when using DHS loading was found to be 0.6 – 2.5 %. A higher PFPH amount will result in a higher PFPH-CH_2O background peak and subsequently higher limit of detection (LOD) and limit of quantification (LOQ) for formaldehyde. But the PFPH/carbonyl ratio needs to be higher than 1.8 to ensure adequate recovery. In our study, loading 144 nmol PFPH onto the tube proved to be a good compromise. The amount can be varied flexibly to meet individual requirements.

Sample Analysis: Plywood and a candle. The feasibility of using PFPH/TD-GC/MS for the determination of formaldehyde was evaluated, including reusability of Tenax TA adsorbent tubes, PFPH-CH_2O background, reproducibility of the DHS loading approach, storage stability after loading, linearity, as well as repeatability of sampling for formaldehyde standards. Several samples were subsequently chosen to demonstrate method feasibility for the determination of formaldehyde and other airborne carbonyls as well as for VOCs and SVOCs. All sampling and analysis steps were performed automatically using the GERSTEL MPS under Maestro® software control.

PFPH loaded Tenax TA tubes can be prepared in advance and stored in the sampler tray. After the analysis and thermal desorption, Tenax TA tubes can be re-used and PFPH freshly loaded just before sampling. Figure 12 and Figure 13 show a schematic of the process steps of the Tenax TA/TD-GC/MS approach and PFPH/TD-GC/MS approach respectively. Again, these can be combined or performed separately.

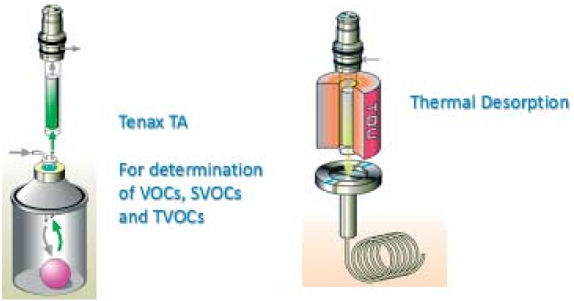

Figure 12. Tenax TA/TD-GC/MS method for the determination of VOCs, SVOCs and TVOC.

Figure 13. PFPH /TD-GC/MS: Schematic diagram of the method used for determination of formaldehyde and other airborne carbonyl compounds.

Plywood and a candle were chosen due to their emission of formaldehyde as reported by authors of previous studies [2,6]. The analysis of E-liquids is reported in a separate application note. Several other sample types were also tested, but no formaldehyde was found, so the results are not reported here.

Plywood. The plywood sample chosen had been shown to exhibit formaldehyde emissions according to previous work based on a DNPH/HPLC method [2]. These had not previously been determined using the PFPH/TD-GC/MS approach. A sample 6 cm x 9 cm in size was prepared and two sides were exposed in a 1 liter micro-scale chamber. More details on the micro-scale chamber system used can be found in previously reported work [2,8]. The sample emission was determined at room temperature.

Figure 14 shows the chromatograms obtained by the Tenax TA/TD-GC/MS and the PFPH/TD-GC/MS approach respectively. It can be seen that significant formation of PFPH-formaldehyde was achieved (peak no. 7) in the bottom chromatogram, which shows that formaldehyde is emitted from this plywood sample. The formaldehyde amount was determined to be 0.26 µg (> LOQ) using external calibration. And the concentration in the micro-chamber was calculated to be 0.51 mg/m^3 based on a sampling volume of 500 mL.

Meanwhile, not only formaldehyde reacted with PFPH, other aldehydes typically emitted by wood based samples, such as pentanal, hexanal, and nonanal had reacted to form PFPH derivatives (peak 1 -> peak 8; peak 2 -> peak 9 & 10; peak 3 -> peak 11). It was found that these four carbonyls reacted quantitatively: No pentanal, hexanal or nonanal was detected in the chromatogram.

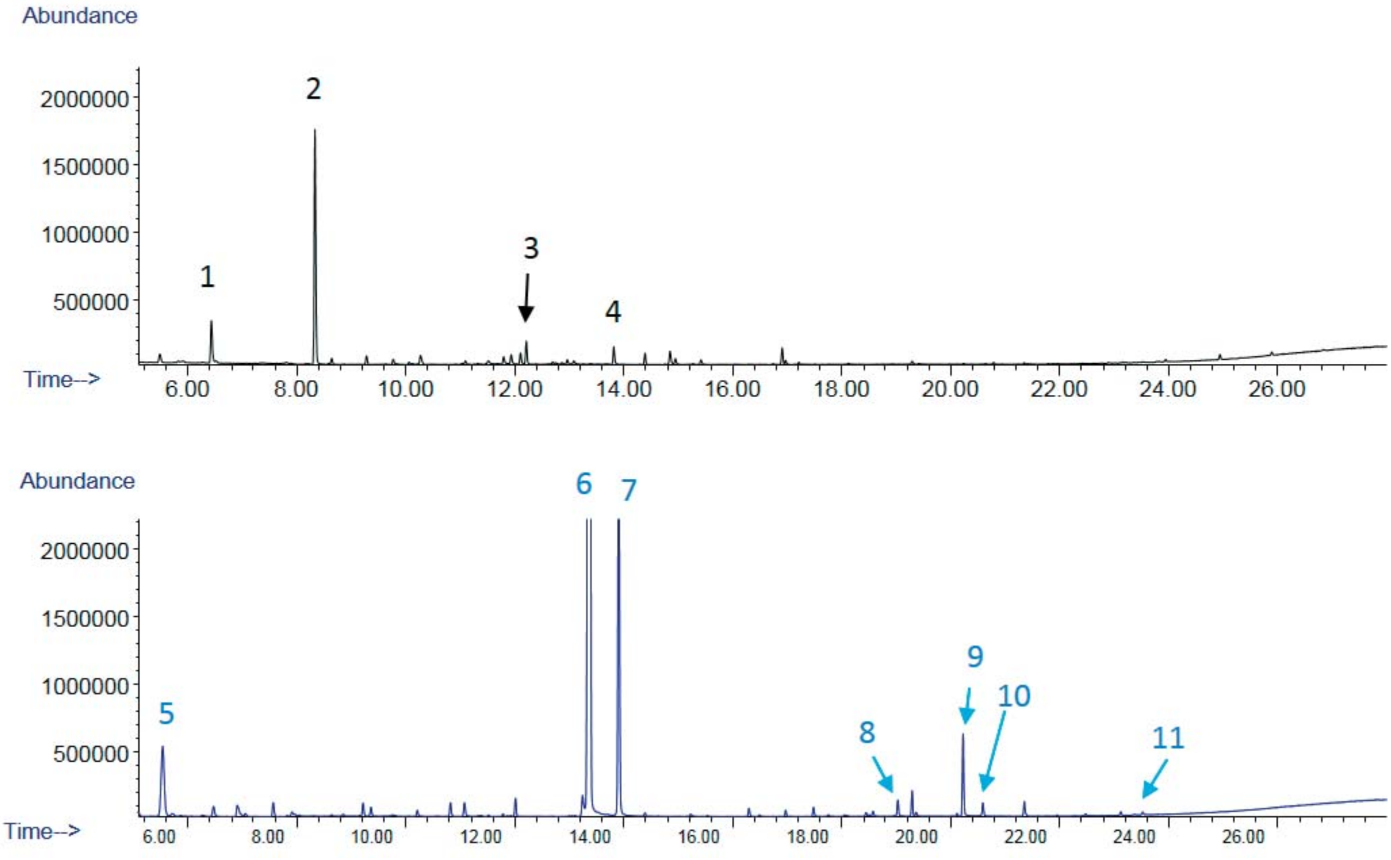

Figure 14. Chromatograms of plywood sample emissions. Top: using a Tenax TA/TD-GC/MS approach, Bottom: using PFPH/TD-GC/MS approach (Incubation temp.: room temp., sampling volume: 1000 mL (top), 500 ml (bottom), CIS initial temp.: -30°C; CIS liner: Tenax TA, split ratio: 1/10 (top), 1/40 (bottom), oven program: : 40°C (2 min) to 280°C (2 min) at 10°C/min).Peak identification: 1.Pentanal, 2. Hexanal, 3. Acetic acid, hexyl ester, 4. Nonanal, 5. Pentafluorobenzene, 6. PFPH, 7. PFPH-formaldehyde, 8. PFPH-pentanal, 9. PFPH-hexanal, 10. PFPH-hexanal isomer, 11. PFPH-nonanal.

EI Mass spectra of the PFPH derivatives are shown in Figure 15. Using GC/MS allowed easy peak identification, especially for isomers such as peak 9 and peak 10 as well as for carbonyls with similar molecular weight. Using the "Extracted Ion Chromatogram" function, PFPH derivatives could be identified much more easily than when using a UV/DAD detector.

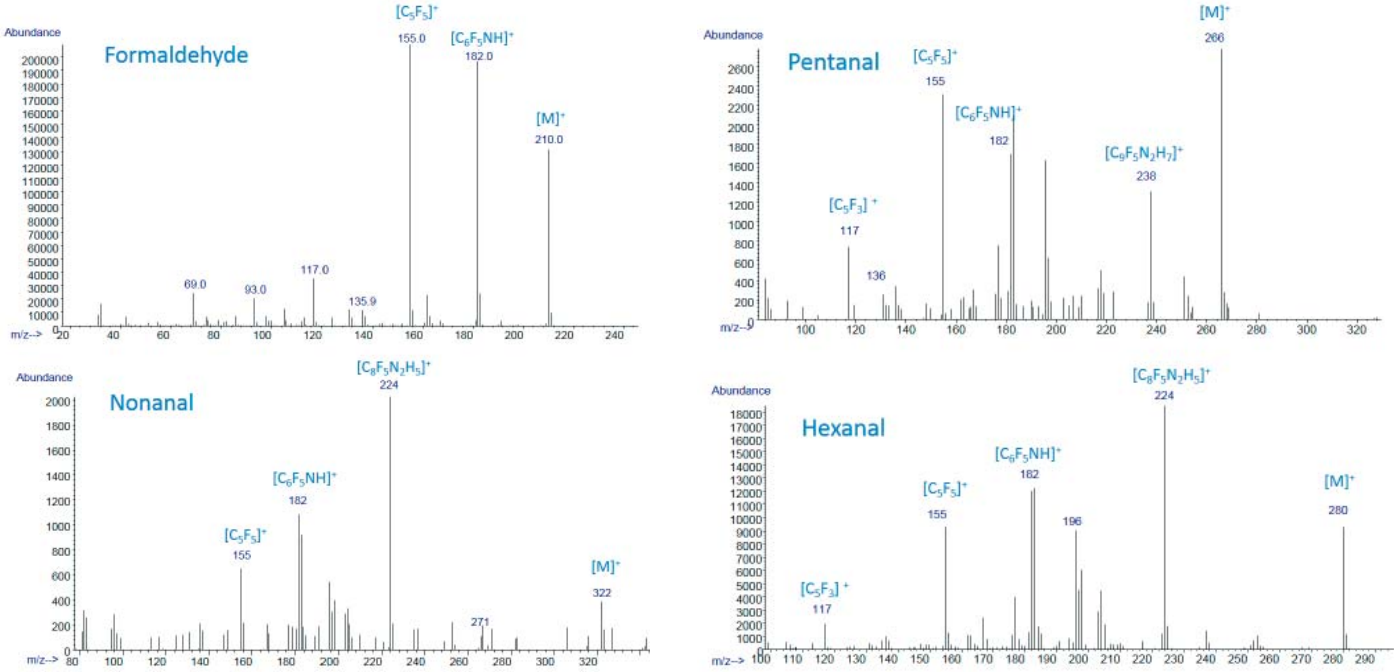

Figure 15. EI mass spectra of the PFPH derivatives of formaldehyde, pentanal, nonanal, and hexanal.

Candle. Candles were identified as another possible formaldehyde emission source [6]. The complete scented block candle analyzed fit directly into a GERSTEL 1 Liter micro-scale chamber without the need to cut it. Sample emissions were determined at room temperature, with a flow rate of 40 mL/min and a sampling volume of 1000 mL for both the Tenax TA/TD- and PFPH/TD methods.

In Figure 16, chromatograms obtained with a Tenax TA tube and with a tube loaded with PFPH respectively are shown. In the top chromatogram, which is based on using Tenax TA adsorbent, many compounds emitted at room temperature from the candle are seen. The main emitted VOCs were added flavor compounds such as ethers and a ketone (alpha-damascone). As an example, ethyl 2-methylbutanoate (peak 3) is found in fruits such as raw and cooked apple, apricot, orange, and grapefruit; isoamyl acetate (peak 5) is found in apple and is present in many fruit aromas, especially banana; 2-methylbutyl acetate (peak 6) is found in apple juice; hexyl acetate (peak 7) has a sweet odor and is also typically found in fruit essences and fruit aroma concentrates; benzyl acetate (peak 11) occurs in jasmine, apple, cherry, and guava fruit and peel (9). But also unwanted compounds were found such as, for example, toluene (peak 1).

Formaldehyde (peak 20) was also detected using the PFPH/TD-GC/MS approach as seen in the chromatogram at the bottom (Figure 16). The determined amount of formaldehyde was 0.095 µg (> LOD) , equal to 0.09 mg/m^3 based on a sample volume of 1 Liter. Equally, some other carbonyls were found to have reacted with PFPH : Peak 2(Hexanal, MW 100) -> peak21 & 22 (PFPH-hexanal and its isomer, MW 280); peak 4 (2-hexanal, MW 98) -> peak 23 (PFPH-2-hexanal, MW 278); peak 9 (Triplal 1, MW 138) -> peak 23 (PFPH-Triplal 1, MW 318); peak 10 (Triplal 2, MW 138) -> peak 24 (PFPH-Triplal 2, MW 318).

The molecular mass difference between a carbonyl and its PFPH derivative is 180, and PFPH derivatives have typical ions at m/z 117, 155, 182, and 183. These have been postulated to be $[C_5F_3]+$, $[C_5F_5]+$, $[C_5F_3NH]+$, and $[C_5F_3NH_2]+$ respectively. These typical ions can be extracted from the chromatogram to find PFPH-carbonyl derivatives. And if the molecular ion of a PFPH-carbonyl is known, the molecular weight of the original carbonyl can be calculated. The original carbonyls can be found using extracted ion chromatograms and identified using a MS library search. This again demonstrates the power of GC/MS for identifying unknown compound.

As can be seen in the two chromatograms in Figure 16, peak responses of compounds that haven't reacted with PFPH are similar. Only peaks, which reacted with PFPH during sampling have been reduced or have disappeared in the PFPH+Tenax TA chromatogram (bottom), e.g. peaks 2, 4, 9 and 10. In these analyses, the same Tenax TA tube was used. After the first run without PFPH, the Tenax TA tube was freshly loaded with PFPH and immediately used for the second analysis. This also proves that PFPH/TD-GC/MS using Tenax TA adsorbent not only provides results for airborne carbonyls, but also for other compounds typically trapped by Tenax TA.

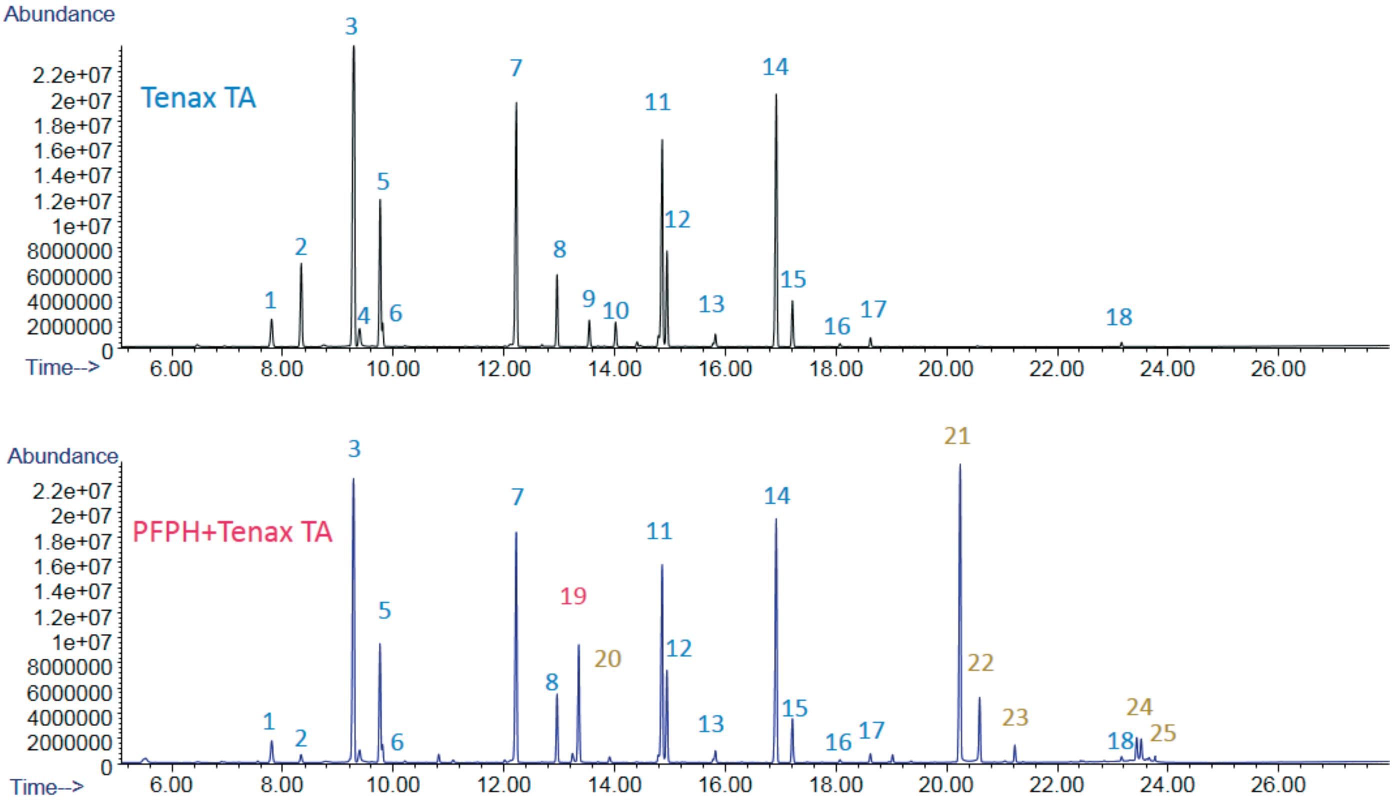

Figure 16. Chromatograms of emissions from a candle sample. Top: using the Tenax TA/TD-GC/MS approach, Bottom: using PFPH/TD-GC/MS approach (incubation temp.: room temp., sampling volume: 1000 mL, CIS initial temp.: -30°C; CIS liner: Tenax TA, split ratio 1/40, oven program: : 40°C (2 min) to 280°C (2 min) at 10°C/min). Peak identification: 1. Toluene, 2. Hexanal, 3. Ethyl 2-methylbutanoate, 4. 2-Hexenal, 5. Isoamyl acetate, 6. 2-Methylbutyl acetate, 7. Hexyl acetate, 8. Isopentyl isobutyrate, 9. Triplal 1, 10. Triplal 2, 11. Benzyl acetate, 12. Ally heptanoate, 13. Isoamyl Allylglycolate, 14. 2-tert-Butylcyclohexanol, 15. 2-tert-Butylcyclohexanol isomer, 16. Alpha-Damascone, 17. Allyl Cyclohexylpropionate, 18. Isopropyl myristate, 19. PFPH, 20. PFPH-formaldehyde, 21. PFPH-hexanal, 22. PFPH-hexanal isomer, 23. PFPH-hexenal, 24. PFPH-Triplal 1, 25. PFPH-Triplal 2.

Conclusion

In this study, we have presented a novel thermal desorption-GC/MS method for determination of formaldehyde emissions from materials using PFPH, automatically loaded onto Tenax TA adsorbent, as derivatization agent. A comparison in terms of performance of the PFPH-TD-GC/MS method and standard DNPH-HPLC/UV methods for the determination of formaldehyde in air is listed in Table 2. The new PFPH-TD-GC/MS method meets the criteria of established international air guidelines (see table 3).

Table 2. Comparison of DNPH-HPLC/UV methods with the new PFPH-TD-GC/MS method.

	DNPH-HPLC/UV		PFPH-TD-GC/MS
Norms	ASTM D5197-09	ISO16000-3	/
HPLC calibration range (µg/mL)	0.5 - 20	0.05 -20	/
DNPH cartridge elution volume [mL Acetonitrile]	6	5	/
Calibration range for formaldehyde (µg)	3-120	0.25-100	0.2 -2
Formaldehyde LOD (µg)			0.09*
Formaldehyde LOQ (µg)			0.25*
Concentration range for Formaldehyde in Air	10 ppb -1 ppm (v/v)	1 µg/m^3-1 mg/m^3	25 µg/m^3 - 2.5 mg/m^3
Sampling volume (L)	not defined	not defined	0.1 - 10

*: according to DIN32645

Table 3. Indoor air guidelines, maximum allowed concentrations for formaldehyde [7].

Organization/Country	WHO, 1987	AgBB	China	USA	France
Formaldehyde conc. (µg/m^3)	100	100	100	3^a-94^b	10^a -50^b

a: Acute/short term
b: Chronic/long term

Air analysis method detection limits depend in general not only on the sensitivity of the detection but also on the sampled volume. The mass flow controllers used in this work cannot conveniently be used for sampling of more than 10 L. Nevertheless, the novel PFPH-TD-GC/MS method presented meets the criteria of established international air guidelines for formaldehyde. Furthermore, the method is meant to be used for material emission studies, for which analyte concentrations are generally much higher.

Among the advantages of the PFPH/TD-GC/MS method are: 1. The user can prepare the tube directly before sampling or can prepare several days' worth of tubes in advance and store them at ambient temperature. 2. Tenax TA adsorbent tubes can be reused several times, reducing cost; 3. Only one GC/MS system is needed for the determination of VVOCs, VOCs and SVOCs. 4 Thermal desorption is highly automated, no manual extraction is needed. 5. High separation power is available when using GC combined with highly specific identification achieved when using an MSD. This means that co-elution can be avoided or easily detected and unknown compounds in complex samples identified. In addition, no solvent is needed for extraction, leading to improved occupational hygiene in the lab, less solvent background in chromatograms and reduced environmental impact. A high degree of automation is achieved based on reusable desorption tubes.

REFERENCES

[1] **Ho, S.S.H. and Yu, J. Zh.** *Determination of Airborne Carbonyls: Comparison of a Thermal Desorption/GC Method with the Standard DNPH/HPLC Method.* s.l. : Enrion. Sci. Thecnol, 2004. pp. 862-870.

[2] **Nie, Y., Lerch, O. and Kleine-Benne, E.** *Determination of Formaldehyde and VOCs in Wood-based Products using an Automated Micro-Scale Chamber.* Mülheim an der Ruhr : GERSTEL AppNote, 2017. No. 193.

[3] **Salthammer, T. and Mentese, S.** *Comparison of analytical techniques for the determination of aldehydes in test chambers.* s.l. : chemosphere, 2008. pp. 1351-1356.

[4] *HJ/T 400-2007: Determination of Volatile Organic Compounds and Carbonyl Compounds in Cabin of Vehicles.* **HJ.** 2007.

[5] **Cecinato, A., et al.** *Pentafluorophenylhydrazine as a coating reagent for the HRGC-MS determination of semi-volatile carbonyl compounds in air.* s.l. : Chromatographia, 2001. pp. 263-269.

[6] **Perkins, M.** *Analysis of Formaldehyde from a Wax Candle Flame suing SIFT-MS.* Cambridge : Anatune Ltd, 2014. AS147.

[7] **Tunga Salthammer, Sibel Mentese, Rainer Marutzky.** *Formaldehyde in the Indoor Environment.* s.l. : Chemical Reviews, 2010. pp. 2536-2572.

GERSTEL GmbH & Co. KG
Eberhard-Gerstel-Platz 1
45473 Mülheim an der Ruhr
Germany
☎ +49 (0) 208 - 7 65 03-0
📠 +49 (0) 208 - 7 65 03 33
@ gerstel@gerstel.com
🌐 www.gerstel.com

GERSTEL Worldwide

GERSTEL, Inc.
701 Digital Drive, Suite J
Linthicum, MD 21090
USA
☎ +1 (410) 247 5885
📠 +1 (410) 247 5887
@ sales@gerstelus.com
🌐 www.gerstelus.com

GERSTEL AG
Wassergrabe 27
CH-6210 Sursee
Switzerland
☎ +41 (41) 9 21 97 23
@ gerstelag@ch.gerstel.com
🌐 www.gerstel.ch

GERSTEL K.K.
1-3-1 Nakane, Meguro-ku
Tokyo 152-0031
SMBC Toritsudai Ekimae Bldg 4F
Japan
☎ +81 3 5731 5321
📠 +81 3 5731 5322
@ info@gerstel.co.jp
🌐 www.gerstel.co.jp

GERSTEL LLP
Level 25, North Tower
One Raffles Quay
Singapore 048583
☎ +65 6622 5486
📠 +65 6622 5999
@ SEA@gerstel.com
🌐 www.gerstel.com

GERSTEL Brasil
Av. Pascoal da Rocha Falcão, 367
04785-000 São Paulo - SP Brasil
☎ +55 (11)5665-8931
📠 +55 (11)5666-9084
@ gerstel-brasil@gerstel.com
🌐 www.gerstel.com.br

ISO 9001
ISO 9001:2008
CERTIFICATE NO. 0086 D

Awarded for the
active pursuit of
environmental sustainability