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

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KEYWORDS

Pentafluorophenylhydrazine (PFPH), Tenax-TA, Dynamic Headspace (DHS), GC/MS, e-liquid, formaldehyde, carbonyl compounds, VOCs

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 e-liquid samples 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 all three samples.

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.

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. [2] 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].

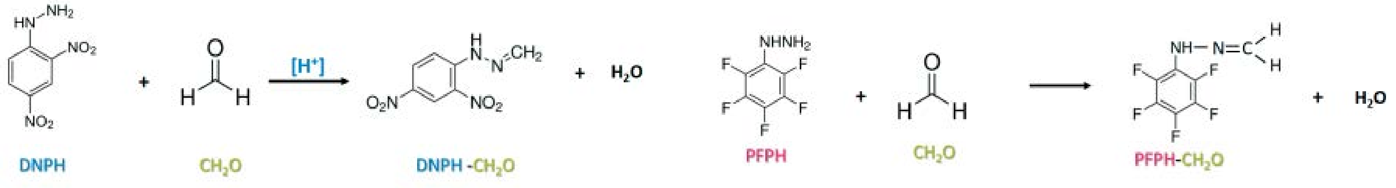

Figure 1. Reaction of DNPH and PFPH with formaldehyde.

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].

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 three e-cigarette liquids, also referred to as e-liquids.

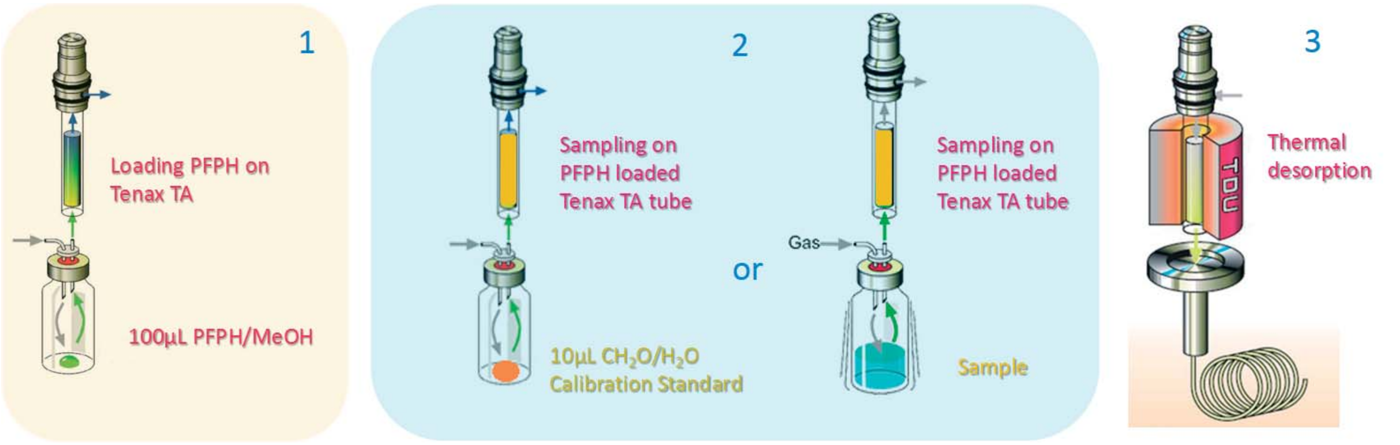

Figure 2. Schematic drawing of the PFPH/TD-GC/MS method steps.

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.

Three different e-liquids, hereinafter referred to as type A, B, and C respectively, were collected from e-cigarette users in the company.

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 analysis of e-cigarette liquids (e-liquids):

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
e-liquid	CH_2O + VOCs	PFPH + Tenax TA	500	40	150	20	1:50

RESULTS AND DISCUSSION

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 4). 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.

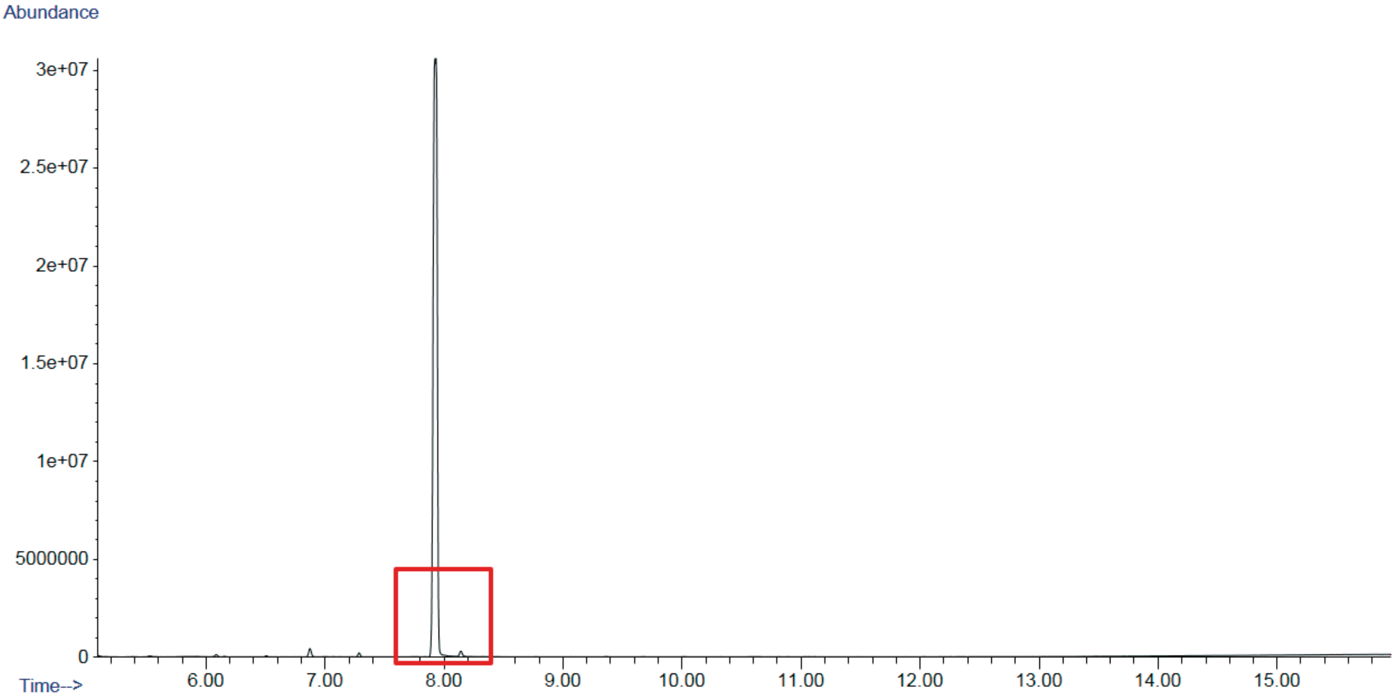

Figure 4. Peaks of PFPH and PFPH-formaldehyde after DHS loading of 100 µL PFPH stock solution and split 1/40.

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 is quantitatively transferred to the tube.

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 5, 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.

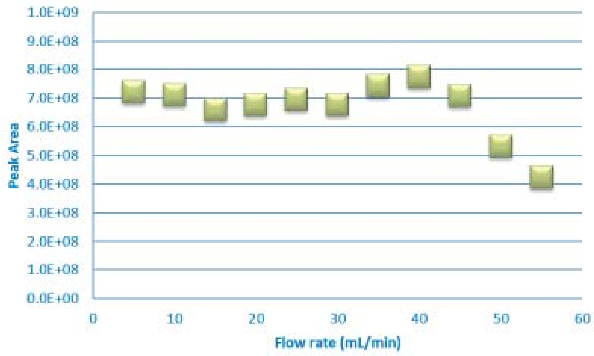

Figure 5. Flow rate optimization for sampling of 10µL formaldehyde/H_2O solution out of a 10 mL vial.

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 6). 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.

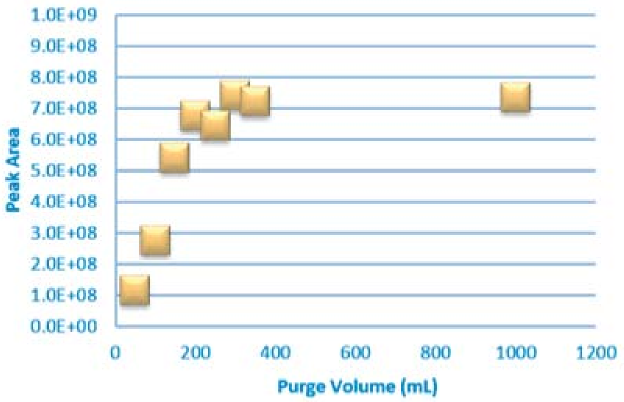

Figure 6. Purge volume optimization for 10µL formaldehyde/H_2O solution in a 10 mL vial.

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 7, 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).

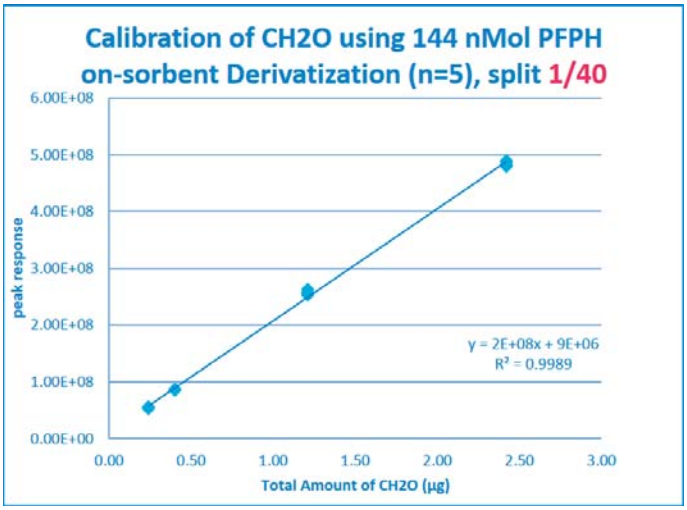

Figure 7. Formaldehyde calibration curve linearity (4 levels, n=5 each).

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: e-cigarette liquids. 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. E-liquids 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 8 and Figure 9 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.

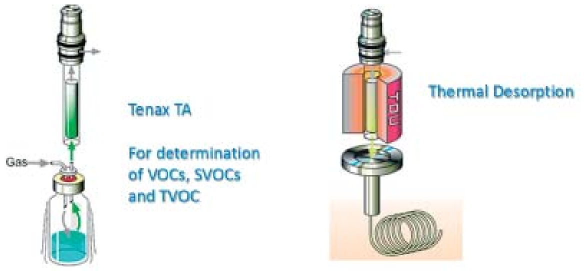

Figure 8. Tenax TA/TD-GC/MS method for the determination of VOCs, SVOCs and TVOC.

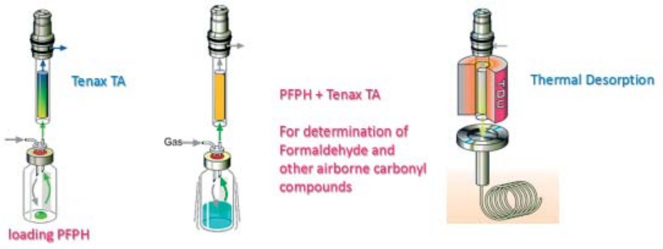

Figure 9. PFPH /TD-GC/MS: Schematic diagram of the method used for determination of formaldehyde and other airborne carbonyl compounds.

E-cigarette liquids were chosen due to their emission of formaldehyde as reported by authors of a previous study [3].

EI Mass spectra of the PFPH derivatives are shown in Figure 10. 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.

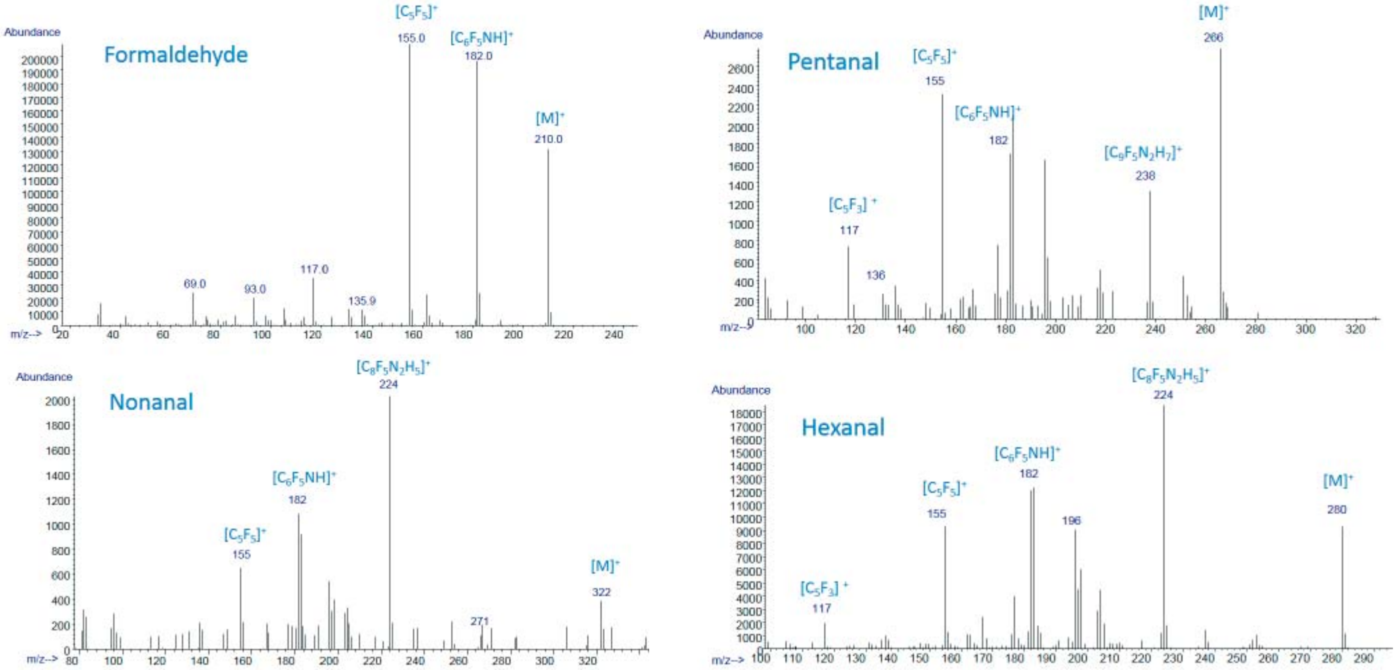

Figure 10. EI mass spectra of the PFPH derivatives of formaldehyde, pentanal, nonanal, and hexanal.

E-liquids. E-cigarettes contain a small battery driven heating unit that vaporizes a mixture of chemicals, called an “e-liquid” [4]. The e-liquid matrix consist of carrier substance (propylene glycol (PG), vegetable glycol (VG) and water). Flavors and different amounts of nicotine are also added into the e-liquid to cater to the tastes of customers.

The vapor released by e-cigarettes was found to contain propylene glycol, glycerol, aerosol particulates and many airborne aldehydes like formaldehyde, acetaldehyde, acrolein, etc. [3-6]. The e-cigarette is considered to be a new source of VOCs and aerosols in indoor air; passive vaping effects have been confirmed.

Unfortunately, the formation of formaldehyde and other carbonyls are unclear; there is a presumption that formaldehyde and acetaldehyde are formed during thermal dehydration of propylene glycol and glycerin [6]. And it has become clear that increasing the voltage applied leads to higher aldehyde emissions [6]. Another study has shown that higher emissions of carbonyls are generated when using e-liquid containing 80 % glycerol and 20 % water instead of “traditional” refill liquids [5]. So e-liquid is a suspected source of formaldehyde.

In our study, three e-liquids were tested, their carrier substances and nicotine concentrations are listed in Table 1. Five microliter samples of each liquid were injected into 10 mL vials and incubated at 150°C during sampling onto individual PFPH loaded Tenax TA tubes. The gas phase volume sampled was 500 mL, collected at a flow rate of 40 mL/min. The adsorbent tubes were held at 40°C during sampling to eliminate water condensation inside the tube.

Table 1. Information on e-liquids and peak areas for formaldehyde and nicotine with RSDs.

E-cigarette liquid	Propylene Glycol/ Vegetable Glycol/water (PG/VG/Water)	Nicotin Conc. (mg/mL)	PFPH-CH$_2$O (m/z 210) Average peak response (RSD %,n=5)	Nicotine Average peak response (RSD %, n=3)
Brand A	50/41/9	0	1.1e+06 (4.3)	0
Brand B	50/41/9	9	3.30E+05	9.8e+07 (2.7)
Brand C	55/35/10	18	2.80E+05	1.7e+08 (5.2)

In Figure 11 three chromatograms obtained from three e-liquids are shown. The main matrix peaks are PG and VG. PFPH-formaldehyde was detected in all three e-liquids, but co-eluted with the VG peaks. m/z 210 was chosen for calculating the PFPH-CH$_2$O amounts. The results are listed in Table 1: Brand A emitted the highest amount of formaldehyde. Five replicate measurements of Brand A were performed, resulting in an RSD of 4.3 %. Nicotine was also detected in some samples, the associated peak areas are listed in Table 1. In the e-liquid Brand C, as specified, the nicotine concentration was found to be twice as high as in Brand B. Repeatability of the nicotine determinations was very good for both samples, RSDs were 2.7 % and 5.2 % respectively (n=3). Additionally, vanillin flavor was found in the Brand B e-liquid. In type A, diacetin and triacetin were detected. Our experiments have shown that dynamic headspace minimizes the amount of PG, GV and water trapped when using Tenax TA adsorbent. The technique works very well compared with direct liquid injection, thermal extraction and the SBSE technique. Similar findings have been reported in a separate study [7].

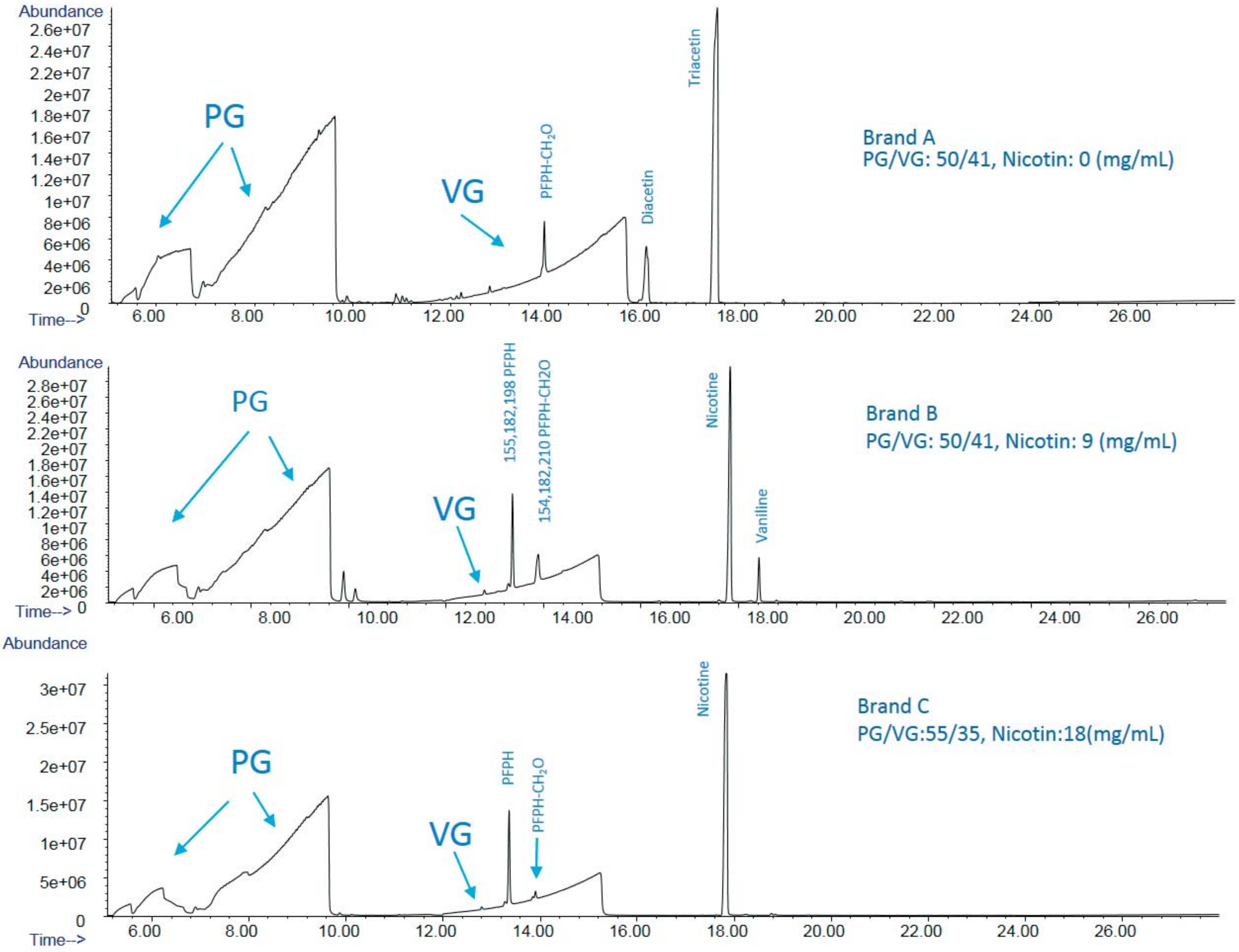

Figure 11. Chromatograms obtained from three e-liquids using PFPH/TD-GC/MS. (sample amount: 5µL, incubation temp.: 150°C, sampling volume: 500 mL, CIS initial temp.: 20°C, CIS liner: Tenax TA, split ratio 1/50, oven program: 40°C (2 min) to 280°C (2 min) at 10°C/min).

CONCLUSION

In this study, we have presented a novel thermal desorption-GC/MS method for determination of formaldehyde using PFPH, automatically loaded onto Tenax TA adsorbent, as derivatization agent.

Formaldehyde was detected in all three e-liquids using PFPH/TD-GC/MS method. And due to using Tenax TA sorbent, matrix, aroma compounds, as well as nicotine were detected in samples. It is also possible to do quantitation using DHS methods.

Among the advantages of the PFPH/TD-GC/MS method, 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. A high degree of automation is achieved based on reusable desorption tubes.

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