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On the use of Carbograph 5TD as an adsorbent for sampling VVOCs: validation of an analytical method†

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A standardised method for the analysis of very volatile organic compounds (VVOCs) in indoor air is still missing. This study evaluates the use of Carbograph 5TD as an adsorbent for 60 compounds (47 VVOCs + 13 VOCs) by comparing their recoveries with different spiking modes. The influence of the spiking of the tubes in dry nitrogen, humidified air or along the whole flushing duration mimicking real sampling was investigated. 49 substances (36 VVOCs from C_1 to C_6) had recoveries over 70% on the adsorbent in humidified air and were validated. The linearity of the calibration curves was verified for every spiking mode and the limits of detection (LOD) and quantification (LOQ) were determined. The LOQs were lower than the existing indoor air guideline values. The robustness of the method was considered by studying the influence of the sampling volume, the sampling flow rate, the humidity level and the storage of the tubes. In general, the most volatile or polar substances were the less robust ones. The combined measurement uncertainty was calculated and lies below 35% for a vast majority of the substances. An example of an emission chamber test using polyurethane foam is shown: Carbograph 5TD performs much better than Tenax® TA for VVOCs and emissions from *n*-butane were quantified with combined measurement uncertainty.

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1 Introduction

Very volatile organic compounds (VVOCs) are ubiquitous in indoor air as they are emitted from human activities, wood and wood-based materials, building materials or indoor chemistry.[1] According to the standards ISO 16000-6 and EN 16516, VVOCs are a group of compounds of the retention range before that of *n*-hexane on a (5%-phenyl)-methylpolysiloxane column.[2,3] ISO 16000-6 describes a procedure for the analysis of VOCs and states that the use of the thermal desorption gas chromatography technique (TD-GC) is appropriate for VVOCs, if adaptations, *inter alia* on the standards, the sampling strategy or GC columns are considered. However, it only gives directions and an efficient procedure for the analysis of VVOCs in indoor air and emission test chamber samples is still lacking. The points that need to be addressed towards the standardization of an analytical method for VVOCs were detailed in our last review article and addressed in our recent publication.[4,5] In the latter, an extensive study of suitable chromatography columns and adsorbents was carried out, which will not be further discussed in this paper.

In the latest study, 16 adsorbents were compared and Carbograph 5TD 40/60 was the most efficient adsorbent with 53 out of 60 substances having a recovery between 70% and 120%. Due to its hydrophobicty, no water management is needed for Carbograph 5TD.[5] The great performance of Carbograph 5TD 40/60 was also observed by Richter *et al.* in 2020, where 27 out of 34 substances had recoveries above 70% at a relative humidity of the sampling air of 50%.[6]

Several studies that compared adsorbents directly with one another also found Carbograph 5TD to be the most appropriate single adsorbent for VVOCs.[7,8] Schieweck *et al.* (2018) demonstrated the use of Carbograph 5TD with a mesh size of 20/40 to adsorb VVOCs with carbon numbers from C_3 to C_6 and validated a method for 18 compounds. In another paper the use of Carbograph 5TD for the analysis of acrolein in indoor air samples is presented.[9] However, this approach only considered a limited number of analytes, and the standards were prepared in methanolic solutions. Moreover, the influence of humidity and the loading of the tube along the whole sampling time were not considered. Indeed, the analytes may behave differently on the adsorbent if they are adsorbed within a few minutes in humidified air compared to when they are spiked all at once in dry nitrogen.

This publication presents extensive experimental results on the evaluation of the use of Carbograph 5TD as an adsorbent for 47 VVOCs and 13 VOCs in gas standards. The recovery of the analytes on the adsorbent was determined in dry nitrogen as

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well as in humidified air, with and without the use of a syringe pump to spike the tube for longer periods of time. The use of liquid standards was also considered for 38 substances. Subsequently, the limits of detection and quantification of the substances were determined. The influence of the sampling volume, the sampling flow rate, the humidity and the storage duration was also studied. Finally, the measurement uncertainty was calculated and an example of quantification from an emission test chamber sample is given.

2 Experimental

2.1 Analysis

2.1.1 Gas standards. The 60 analytes were divided into three gas mixtures as presented in Table 1. They were selected because of their appearance in indoor air studies or the availability of either guideline values or toxicological properties (see ESI Table S1†). 13 compounds are VOCs according to ISO 16000-6 (ref. 2) but were chosen as compounds of the transition region between the VVOC and VOC ranges. For the most volatile compounds, commercial gas mixtures were custom produced in pressurized gas cylinders by Linde GmbH (Unterschleißheim, Germany) at a target concentration of 1000 ppm in nitrogen. The chlorinated hydrocarbons were prepared in a separate mixture to prevent reactions with the other substances. These mixtures were filled into gas collecting tubes (GCTs) under a fume hood for further handling. The GCT consists of an elongated gas-tight container made of glass with a valve at each end. They are additionally equipped with a septum for the injection of the compound mixtures.

Table 1 Composition of gas mixtures with corresponding calibration ranges of the analytes (detailed in Table S2 of the ESI)

				Commercial gas mixture 1 (CGM1)		
Group	CAS	Substance	Cal range (ng)	CAS	Substance	Cal range (ng)
1	67-56-1	Methanol[b]	0.4–160	115-07-1	Propene[b]	0.3–153
	64-17-5	Ethanol[b]	0.4–162	75-19-4	Cyclopropane[b]	0.3–160
	67-63-0	Isopropanol	0.2–96	115-10-6	Dimethyl ether[b]	0.3–172
	75-65-0	*tert*-Butanol	0.2–100	106-99-0	1,3-Butadiene	0.4–196
	71-23-8	1-Propanol	0.4–162	75-28-5	Isobutane	0.5–218
	75-15-0	Carbon disulfide	0.2–87	106-97-8	*n*-Butane	0.5–222
	71-43-2	Benzene[a]	0.2–72	624-64-6	*trans*-2-butene	0.5–219
2	79-20-9	Methyl acetate	0.4.-185	590-18-1	*cis*-2-butene	0.5–214
	108-05-4	Vinyl acetate	0.4–165	75-07-0	Acetaldehyde[b]	0.4–175
	141-78-6	Ethyl acetate[a]	0.3–148	78-78-4	Isopentane	0.6–269
	108-21-4	Isopropyl acetate[a]	0.3–141	109-66-0	*n*-Pentane	0.6–268
	107-31-3	Methyl formate[b]	0.4–160	107-02-8	Acrolein	0.5–212
3	67-64-1	Acetone	0.3–129	110-54-3	*n*-Hexane	0.7–317
	78-93-3	2-Butanone	0.2–110			
	96-33-3	Methyl acrylate[a]	0.2–92	**Commercial gas mixture 2 (CGM2)**		
4	78-79-5	Isoprene	0.2–112	**CAS**	**Substance**	**Cal range (ng)**
	287-92-3	Cyclopentane	0.2–82	75-45-6	Chlorodifluoromethane[b]	0.8–190
	107-83-5	2-Methylpentane	0.2–80	74-87-3	Chloromethane[b]	0.4–99
5	123-38-6	Propanal	0.4–188	75-01-4	Vinyl chloride[b]	0.5–136
	110-62-3	Pentanal[a]	0.2–112	75-71-8	Dichlorodifluoromethane	1.0–239
	78-84-2	Isobutanal	0.2–97	75-00-3	Chloroethane	0.5–131
	78-85-3	Methacrolein	0.3–120	75-69-4	Trichlorofluoromethane	0.5–290
	123-72-8	Butanal[a]	0.3–118	75-29-6	2-Chloropropane	0.7–164
6	110-00-9	Furan	0.2–95	67-66-3	Chloroform[a]	0.2–75
	60-29-7	Diethyl ether	0.3–120			
	109-99-9	Tetrahydrofuran[a]	0.2–95	**Internal gas standard**		
	123-91-1	1,4-Dioxane[a]	0.2–93	**CAS**	**Substance**	**Amount (ng)**
	1634-04-4	Methyl *tert*-butyl ether	0.2–99	1076-43-3	Benzene-d_6	18.6
7	107-13-1	Acrylonitrile	0.2–79			
	75-05-8	Acetonitrile[b]	0.2–79			
	126-98-7	Methacrylonitrile	0.2–80			
	107-12-0	Propanenitrile	0.2–77			
8	56-23-5	Tetrachloromethane[a]	0.2–76			
	107-06-2	1,2-Dichloroethane[a]	0.2–77			
	75-35-4	1,1-Dichloroethene	0.1–66			
	74-96-4	Bromoethane	0.3–129			
	75-09-2	Dichloromethane	0.3–118			
	79-01-6	Trichloroethene[a]	0.2–80			
As ISTD	142-82-5	*n*-Heptane[a]	0.2–75			

[a] Substances that do not belong to the group of VVOCs according to the definition of ISO 16000-6 and EN 16516. [b] Substances that could not be validated in this study.

The other 39 compounds were part of a self-made gas mixture. It was prepared in a gas collecting tube with a volume of 437.6 mL (commercially given as 500 mL) and equipped with a septum and a valve for additional tightness. The liquid standards were mixed with syringes into eight groups of solutions (see Table 1) to a total volume of 1500 or 3000 μL to increase spiking accuracy without creating possible reactivity in each solution. Small defined volumes of *n*-heptane were added to each group: being in the upper volatility range and non-reactive, a change in the ratio of the compounds to *n*-heptane is indicative of leakage or reactivity. In this way, *n*-heptane served as an additional safeguard but was not used in the determination of the evaluation parameters as described in the following section. The groups were then spiked with a gas-tight syringe (Hamilton, Reno, Nevada, USA) through the septum of the GCT where the substances evaporate into the gas phase. The stock solutions were stored in a freezer at −18 °C.

Benzene-d_6 served as an internal standard (ISTD): a gas standard was manufactured in-house with a concentration of 266 ppm in nitrogen in a pressurized cylinder, and a gas collecting tube (GCT) was filled with it for further handling. The reactivity and stability of the gas mixtures were checked.[5] The spiking of gas mixtures was compared to the spiking of methanolic solutions. For this purpose, the liquid standards used for the self-made gas mixture were directly diluted in methanol.

2.1.2 Adsorbent tubes. TDS (thermal desorption system) glass tubes from Gerstel (Mülheim an der Ruhr, Germany) were filled with Carbograph 5TD with a mesh size of 40/60 from Markes (Bridgend, United Kingdom) to an approximate bed length of 6 cm, corresponding to a mean weight of 326 mg. Prior to use, the tubes were conditioned in a tube conditioner from Gerstel at 350 °C with a nitrogen flow of approximately 80 mL min^{-1} for at least three hours.

Tenax® TA tubes from Gerstel were also used for comparison and conditioned at 300 °C.

2.1.3 Adsorbent spiking. The tubes were always doped with 20 μL of the ISTD gas mixture (18.6 ng) first. This took place with a 25 μL gas-tight syringe (Hamilton, Switzerland) on a tube standard preparation system (TSPS, Gerstel) before each analysis. They were then shortly flushed with dry nitrogen (ALPHAGAZ – Air Liquide) at 23 ± 2 °C and 80 ± 2 mL min^{-1}.

The tubes were subsequently doped with the gas mixture by use of gas-tight syringes (Hamilton, Switzerland) with volumes of 10 to 250 μL, depending on the calibration point. The calibration ranges are displayed in Table 1 and detailed in ESI Table S2.† The adsorbents were then flushed at 23 ± 2 °C and 80 ± 2 mL min^{-1} using different spiking modes:

- manually on a TSPS and flushed in parallel with dry nitrogen for 10 min,
- manually on a spiking device different from the TSPS and subsequently flushed with humidified synthetic air at 50 ± 5% RH for 10 min,
- with a syringe pump to mimic a real sampling: the gas mixture was automatically spiked onto the adsorbent for 9 min while a humidified air flow (50 ± 5% RH) was passed through the tube for 10 min (additional 1 min after spiking).
- manually on a TSPS and flushed with dry nitrogen for 3 min. Subsequently, humidified air (50 ± 5% RH) from an empty emission chamber was drawn through the tubes with a pump for 10 min. This method allowed a high sample throughput, as six tubes could be simultaneously spiked on the TSPS and the humidified air could be drawn through six tubes simultaneously thanks to a multiple pump. Thus, it was used for the validation of the method (limits of detection and quantification, robustness and measurement uncertainty).

2.1.4 Thermal desorption. An automated thermal desorption system (TDS3/TDSA, Gerstel) connected to a cold injection system (CIS4, Gerstel) was used at one of the two injection ports of the GC. The spiked adsorbents were automatically loaded by the TDSA and thermally desorbed in the TDS3, which was flown through with helium (ALPHAGAZ – Air Liquide, Düsseldorf, Germany) as the carrier gas at 50 mL min^{-1}. It was programmed to start at 35 °C and heated up with a rate of 60 °C s^{-1} to 350 °C and held for 5 min. During thermal desorption, analytes were cryotrapped at −150 °C using liquid nitrogen from Linde in the CIS4 equipped with a liner filled with deactivated glass wool (Gerstel). The CIS4 was then flushed with helium (ALPHAGAZ – Air Liquide), heated up to 250 °C at 12 °C s^{-1} and finally held at 250 °C for 5 min for complete transfer into the GC. The TDS-CIS system was used in solvent vent mode to allow both TDS and CIS to be operated in splitless mode.

Tenax® TA tubes from Gerstel were desorbed at 300 °C with the same method.

2.1.5 Direct injection. A Merlin Microseal (Agilent Technologies, Waldbronn, Germany) was mounted on the split/splitless injector of a 7890A GC from Agilent Technologies. The Merlin Microseal was selected to avoid injector leaks through coring as well as septum residues leading to obstruction of the syringe and active sites in the liner. A split/splitless liner with a diameter of 2 mm was used. The gas mixture was injected directly with a gas-tight syringe into the split/splitless injector, and the run was started. The injector was kept at a temperature of 250 °C.

2.1.6 GC/MS parameters. A PoraBOND Q (50 m, 0.32 mm, 5 μm) column was considered because it had been selected as the most adapted column for VVOC analytics in a previous study.[5] It was flushed with helium (ALPHAGAZ – Air Liquide) as the carrier gas at 3.2 mL min^{-1} in constant flow mode. A deactivated GC capillary (10 m length, 0.25 mm diameter) was installed between the column and the MS, which served as a particle trap, and the column and the capillary were connected *via* a SilTite μ-Union from Trajan (Sprockhövel, Germany). The GC oven temperature program started with 35 °C for 1 min, then heated up to 80 °C at 8 °C min^{-1}, held for 1 min at 80 °C and then heated to 230 °C at 5 °C min^{-1}.

A mass selective detector MSD 5975C inert XL from Agilent Technologies was connected to the GC. The temperatures of the transfer line, quadrupole, and ion source were 300 °C, 150 °C, and 230 °C, respectively. The MS was operated in full-scan mode: the *m*/*z* scan range was between 29 and 150 and a low

mass tune was performed. With the selected column (PoraBOND Q), the lower m/z was only necessary for the early-eluting analytes. Thus, the scan started at m/z 35 after 12.5 min.

The retention times and quantifier ions used are displayed in Table S3 ESI.† Blank values of the tubes were subtracted before data analysis: for tubes spiked in dry nitrogen, the analysis of the unloaded tube was considered, whereas for tubes spiked in humidified air, the air sampled from an empty emission test chamber on the same tube was considered. Data were processed by using the MassHunter Quant Software (version 10.2, Agilent). An example chromatogram is depicted in ESI Fig. S1.†

2.2 Validation

2.2.1 Recovery. For the determination of the recovery of the 60 analytes, the results of the direct injection of the gas mixture were compared to those of the thermal desorption of the spiked tubes, like in previous studies,[5,6] following eqn (1):

$$\text{Recovery}_{\text{Analyte}} = \frac{\frac{A_{\text{Analyte, spiked tube}} - A_{\text{Analyte, blank tube}}}{A_{\text{ISTD, spiked tube}}}_{\text{TD}}}{\sum\left(\frac{A_{\text{Analyte}}}{A_{\text{ISTD}}}_{\text{N direct injections}}\right)\Big/N} \times 100 \quad (1)$$

where A stands for signal area, ISTD for the internal standard, TD for thermal desorption, and N is the number of direct injection analyses carried out.

The recoveries were determined with the doped amount corresponding to the calibration level Cal 9 (see Table S2 ESI†). A recovery of 70% to 120% was indicative of a satisfying adsorption of the analyte on the tube.[10]

2.2.2 Determination of limits of detection and quantification. The decision limit, detection limit (LOD) and determination limit (or limit of quantification – LOQ) were determined according to DIN 32645 (ref. 11) with the indirect method: ten equidistant points with volumes of the gas mixtures between 0.2 and 2.0 μL were spiked onto the adsorbents (corresponding to Cal 1 and Cal 4 for the self-made gas mixture and commercial gas mixture 1 and between Cal 1 and Cal 5 for the commercial gas mixture 2). A significance level of 95% and an uncertainty of 25% ($k = 4$) were considered.

For 14 substances, the decision limit was beyond the calibration range from the indirect method and another method was used. The LOD and LOQ were calculated as described in the Eurachem guide to method validation:[12]

$$\text{LOD} = 3 \times \frac{\text{STDEV(Cal1, } n \text{ measurements)}}{\sqrt{n}} \quad (2)$$

$$\text{LOQ}_1 = 10 \times \frac{\text{STDEV(Cal1, } n \text{ measurements)}}{\sqrt{n}} \quad (3)$$

where n is the number of measurements of the lowest calibration level Cal 1 (10).

As the value of the LOQ determined with this method seems to be too low compared to the observed calibration curves for the lower calibration levels, another definition is proposed for the LOQ: the limit of quantification (LOQ_2) was the lowest calibration level n for which the correlation coefficient of the calibration Cal1–Cal$n$ was greater than 0.99.

2.2.3 Robustness. The robustness of the method was studied by varying the doping parameters as listed below. ISO 16000-6 and EN 16516, respectively, require sampling volumes normally starting from 1 L. However, depending on the analytes and particularly for VVOCs, lower sampling volumes can be useful. For this study, we chose to compare the investigated parameters against a sampling volume of 0.8 L taken at a flow rate of 80 mL min^{-1} at a relative humidity of 50% (see Section 3.3).

- Sampling volume: 0.8, 1.6 and 4.0 L at a sampling flow rate of 80 mL min^{-1}
- Sampling flow rate: 40, 80 and 120 mL min^{-1} at a sample volume of 0.8 L
- Relative humidity: 30, 50 and 70% RH at 0.8 L and 80 mL min^{-1}

Moreover, the influence of the stability of the analytes in the tubes was examined by analyzing them 7, 14 and 28 days after spiking and storage at (23 ± 2) °C.

2.2.4 Measurement uncertainty. The expanded measurement uncertainty for the mass of the analyte in the air sample was calculated by combining the uncertainty budgets as shown in eqn (4) and following the recommendations in ref. 13

$$\frac{u(m_{\text{Calculated}})}{m_{\text{Calculated}}} = k \times \sqrt{\left(\frac{u(c_{\text{GCT}})}{c_{\text{GCT}}}\right)^2 + u_{\%}(\text{tube spiking})^2 + \left(\frac{u(\text{cal})}{m_{\text{calculated}}}\right)^2 + \left(\frac{u(\text{prec})}{m_{\text{calculated}}}\right)^2} \quad (4)$$

where u is the uncertainty, $m_{\text{Calculated}}$ is the result of the analysis, *i.e.* mass of the analyte in the air sample, calculated *via* the calibration equation, k is the safety coefficient (here $k = 2$ for a 95% confidence level), c_{GCT} is the concentration of the analyte in the GCT, u(tube doping, %) is the uncertainty of the tube doping, u(cal) is the uncertainty of the calibration, and u(prec) is the method precision.

The budgets are determined as follows:

For analytes from the self-made gas standard, the uncertainty of the analyte concentration in the GCT was calculated as follows:

$$\frac{u(c_{GCT})}{c_{GCT}} = \sqrt{u_{\%}(pur)^2 + u_{\%}(syr_1)^2 + \frac{u_{\%}(syr_1)^2 \times \sum V_i^2}{\sum V_i} + u_{\%}(syr_2)^2 + u_{\%}(V_{GCT})^2 + u_{\%}(prep)} \quad (5)$$

where pur is the purity of the analyte, syr_1 is the syringe used for preparation of the liquid solution, syr_2 is the syringe used for GCT doping, V_i is the volume of every analyte i of the considered group (see Table 1), V_{GCT} is the volume of the GCT, and $u_{\%}$(prep) is the standard deviation from three repetitions of gas mixture preparations with solutions prepared in three different years (2020, 2021, and 2022), and kept in the freezer. Within one week, aliquots from all solutions were doped into the GCT and analyses were performed by direct injection.

For analytes from the commercial gas mixtures, the uncertainty of the analyte concentration in the GCT was calculated as follows:

$$\frac{u(c_{GCT})}{c_{GCT}} = \sqrt{u_{\%}(mix)^2 + u_{\%}(fill)^2} \quad (6)$$

where $u_{\%}$(mix) is the uncertainty of the gas mixture given in the certificate and $u_{\%}$(fill) is the uncertainty determined as the standard deviation from three fillings of the commercial gas mixtures into the GCT (within one week). The analyses were performed by direct injection.

As human error from the doping of the tube is already considered in the measurement precision (see below), the uncertainty from the tube spiking was only the bias of the syringe.

The uncertainty from the calibration was calculated as follows:[13]

$$u(Cal) = \frac{S}{B} \times \sqrt{\frac{1}{p} + \frac{1}{n} + \frac{(m_{calculated} - \bar{m})}{\sum(m_i - \bar{m})}} \quad (7)$$

where S is the residual standard deviation, B is the slope of the calibration curve, p is the number of measurements to determine $m_{calculated}$, n is the number of calibration levels, $m_{calculated}$ is the determined amount, $\bar{m}$ is the mean value of the different calibration amounts, and m_i is the calibration level.

In accordance with ref. 14, the method precision u(prec) (eqn (8)) is calculated by using a combination of the repeatability u(rep) (eqn (9)) and the reproducibility u(repr) (eqn(10)):

$$u(Prec) = \sqrt{u(rep)^2 + u(repr)^2}, \quad (8)$$

with:

$$u(rep) = \sqrt{\frac{\sum STDEV_i^2}{n_{meas}} + \frac{\sum(\bar{m}_i - \bar{m}_{tot})^2}{n_{meas} - 1}} \quad (9)$$

where u(rep) is the uncertainty of the repeatability, $STDEV_i$ is the standard deviation of the measurements on day i (5 days), n_{meas} is the total number of measurements (21), $\bar{m}_i$ is the average of the measurement on day i, and $\bar{m}_{tot}$ is the average of all measurements; and

$$u(repr) = \sqrt{\frac{STDEV_1^2 + STDEV_2^2}{n_{repr}}} \quad (10)$$

where u(repr) is the reproducibility, $STDEV_{1,2}$ is the standard deviation of the measurements of workers 1 and 2, and n_{repr} is the total number of measurements (12).

Of note, the uncertainty of the GC/MS measurement is considered three times in this combined measurement uncertainty ($u(V_{CGCT},\%)$, u(rep) and u(repr)). However, it is inevitable as these uncertainties are all determined from measurements.

2.3 Emission chamber measurement

Polyurethane foam was applied in an aluminum bowl. The sample was placed in a 270 L emission test chamber made of stainless steel, equipped with a ventilator. It was operated in compliance with EN 16516 ref. 3 at a temperature of (23 ± 1) °C, a relative humidity of (50 ± 5)% and an air change rate of 0.5 h^{-1}. The air samples were simultaneously taken after 7 days with a pump at 100 mL min^{-1} during 10 min. Pictures from the sample and the emission test chamber are shown in ESI Fig. S2.†

3 Results and discussion

3.1 Recoveries

The recoveries of the 60 analytes following different doping modes are displayed in Fig. 1. For the recoveries in dry nitrogen, the results of our previous work were confirmed:[5] under the conditions selected for this study, *i.e.* with 0.8 L gas passing through the sorbent tube during analyte loading, 51 out of 60 substances showed recoveries over 70%. Only methyl acrylate had a very low value (17 ± 2%) compared to the last study (95 ± 9%). The reason for this striking change is unknown. However, methyl acrylate had much better recoveries (over 70%) for doping modes in humidified air, and this is also the case for dichlorodifluoroethane. These substances were therefore selected for further validation. Substances with recoveries over 70% for both spiking modes with humidified air [spiking device in Fig. 1b and syringe pump in Fig. 1c] were chosen for the method validation.

Following this criterion, the method cannot be validated for 11 substances: chlorodifluoromethane, methanol, propene, chloromethane, cyclopropane, dimethylether, acetaldehyde, vinyl chloride, methyl formate, ethanol and acetonitrile. These substances have either very high volatilities or very high polarities. Interestingly, methanol, dimethyl ether, acetaldehyde, and acetonitrile had very poor recoveries in humidified air in comparison to their satisfactory recoveries in dry nitrogen. They all have a very high affinity to water (see log K_{ow} values in Table S1 of the ESI†), so it is logical that they adsorb much less on the

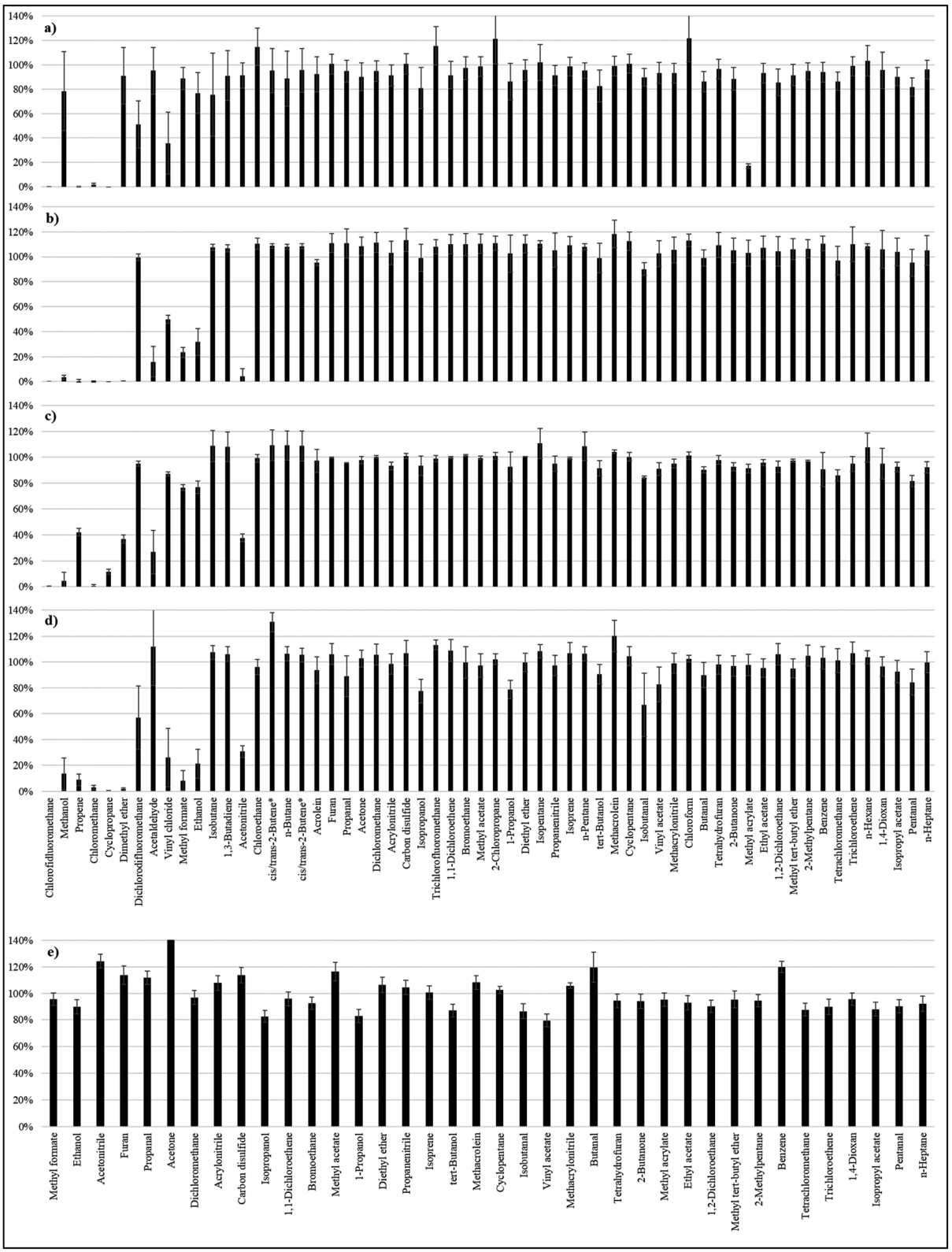

Fig. 1 Recoveries of the 60 analytes on Carbograph 5TD following different spiking modes: (a) spiking of the tube in dry nitrogen ($n = 15$), (b) spiking of the tube in humidified air ($n = 3$), (b) spiking of the tube in humidified air over 9 min with a syringe pump ($n = 3$), (d) short spiking of the tube in dry nitrogen followed by flushing with humidified air ($n = 3$), and (e) spiking of liquid standards in dry nitrogen ($n = 3$). The sample volume in all cases was 0.8 L.

adsorbent when water is present in the air flow. In comparison, ethanol, vinyl chloride and methyl formate had high recoveries in humidified air when a syringe pump was used, whereas they had poor recoveries when the gas mixture was injected at once. In this case, the substances are either less volatile or less polar than the previous ones: the adsorption is efficient when the gas mixture is doped throughout the whole flushing time but a breakthrough seems to appear when the substances are spiked in the first few seconds. One likely explanation for this is that a spiking of the analytes at once introduces a more concentrated band of the compounds which can therefore more quickly saturate the active sites in the affected section of the sorbent causing more rapid movement through the sorbent bed. The other unvalidated substances chlorodifluoromethane, propene, chloromethane and cyclopropane showed recoveries below 70% with each spiking mode. In a previous study, ethanol and acetaldehyde were validated but the tubes were only spiked in dry nitrogen.[8] It can be concluded that Carbograph 5TD is well suitable for compounds with carbon numbers in the range of C_3–C_6. However, this must not be taken as a general rule as compounds with 3 carbon atoms such as cyclopropane or propene did not adsorb on the adsorbent while compounds with only one or two carbon atoms such as tetrachloromethane or bromoethane did.

Fig. 1e displays the recoveries for the spiking of the methanolic solutions of the standards on the adsorbent. Even if polar substances typically had lower recoveries than nonpolar ones, all the validated substances displayed recoveries between 79 and 120%, except for acetone. In principle, methanolic solutions would lead to similar quantification results in comparison to gas mixtures but the use of a solvent has several drawbacks as reported elsewhere.[4]

3.2 Calibrations

The coefficients of determination of the calibrations of the 49 validated substances with different spiking modes are shown in Table 2. Example of calibration curves for each gas mixture are displayed in Fig. S3 ESI.† Except for dichlorofluoromethane, all the substances had coefficients of determination over 0.99 when spiked with humidified air. The poor coefficients of determination for dichlorofluoromethane (still over 0.98) were due to high standard deviations of the signal (poor precision, see Section 3.5.). 2-Chloropropane, cyclopentane and isobutanal had a coefficient of determination below 0.99 for the calibration in dry nitrogen (b). These results are due to the high number of repetitions (from $n = 4$ to $n = 19$ depending on the calibration level, over three months) while other calibrations were only based on three repetitions over two weeks. For real samples, the calibration would be repeated more often and these compounds performed much better in these later calibrations in humidified air (c, d and e), indicating the suitability of the method.

Interestingly, ethanol, vinyl chloride and methyl formate which had high recoveries in humidified air when a syringe pump was used (see Section 3.1.), displayed satisfactory calibration curves for this spiking mode (see ESI Fig. S4†). However, they were not considered for further validation as the spiking mode with a short spiking in dry nitrogen and a longer flushing with humidified air was used.

Table 2 Coefficients of determination of the calibrations (Cal1–Cal12) of the 49 validated substances, with different spiking modes: (a) direct injection of the gas standard on the GC column (n = min 3), (b) spiking of the tube in dry nitrogen (n = min 4), (c) spiking of the tube in humidified air (n = 3), (d) spiking of the tube in humidified air over 9 min with a syringe pump (n = min 3), and (e) short spiking of the tube in dry nitrogen followed by flushing with humidified air (n = 3). The sample volume in all cases was 0.8 L

	a	*B*	*c*	*d*	*e*
Dichlorodifluoromethane	0.9988	0.9821	0.9839	0.9883	0.9818
Isobutane	0.9982	0.9911	0.9993	0.9969	0.9999
1.3-Butadiene	0.9984	0.9973	0.9991	0.9972	0.9998
Chloroethane	0.9993	0.9911	0.9989	0.9937	0.9927
cis/*trans*-2-butene[a]	0.9986	0.9959	0.9991	0.9972	0.9998
n-Butane	0.9979	0.9958	0.9988	0.9966	0.9997
cis/*trans*-2-butene[a]	0.9991	0.9969	0.9995	0.9977	0.9999
Acrolein	0.9994	0.9935	0.9979	0.9922	0.9999
Furan	0.9975	0.9946	0.9992	0.9933	0.9959
Propanal	0.9981	0.9910	0.9997	0.9963	0.9976
Acetone	0.9976	0.9992	0.9993	0.9928	0.9936
Dichloromethane	0.9980	0.9977	0.9994	0.9940	0.9946
Acrylonitrile	0.9988	0.9970	0.9998	0.9955	0.9966
Carbon disulfide	0.9956	0.9951	0.9967	0.9929	0.9934
Isopropanol	0.9987	0.9967	0.9995	0.9937	0.9935
Trichlorofluoromethane	0.9986	0.9913	0.9994	0.9928	0.9987
1.1-Dichloroethene	0.9979	0.9984	0.9995	0.9944	0.9965
Bromoethane	0.9978	0.9953	0.9996	0.9942	0.9977
Methyl acetate	0.9985	0.9958	0.9997	0.9953	0.9958
2-Chloropropane	0.9990	0.9841	0.9997	0.9945	0.9998
1-Propanol	0.9985	0.9980	0.9988	0.9917	0.9946
Diethyl ether	0.9979	0.9976	0.9994	0.9944	0.9958
Isopentane	0.9988	0.9952	0.9996	0.9981	0.9998
Propanenitrile	0.9985	0.9967	0.9995	0.9940	0.9959
Isoprene	0.9984	0.9924	0.9996	0.9947	0.9971
n-Pentane	0.9979	0.9968	0.9991	0.9975	0.9995
tert-Butanol	0.9975	0.9974	0.9995	0.9947	0.9961
Methacrolein	0.9973	0.9979	0.9989	0.9913	0.9919
Cyclopentane	0.9987	0.9854	0.9998	0.9960	0.9983
Isobutanal	0.9987	0.9641	0.9991	0.9959	0.9991
Vinyl acetate	0.9983	0.9902	0.9994	0.9953	0.9972
Methacrylonitrile	0.9983	0.9940	0.9998	0.9957	0.9962
Chloroform	0.9976	0.9906	0.9981	0.9921	0.9987
Butanal	0.9973	0.9973	0.9992	0.9960	0.9925
Tetrahydrofuran	0.9988	0.9959	0.9997	0.9964	0.9953
2-Butanone	0.9982	0.9991	0.9996	0.9963	0.9944
Methyl acrylate	0.9976	0.9991	0.9997	0.9958	0.9957
Ethyl acetate	0.9979	0.9970	0.9997	0.9955	0.9953
1.2-Dichloroethane	0.9972	0.9987	0.9996	0.9953	0.9951
Methyl *tert*-butyl ether	0.9986	0.9972	0.9998	0.9952	0.9966
2-Methylpentane	0.9985	0.9953	0.9998	0.9963	0.9976
Benzene	0.9966	0.9904	0.9966	0.9925	0.9930
Tetrachloromethane	0.9971	0.9962	0.9990	0.9938	0.9971
Trichloroethene	0.9944	0.9948	0.9989	0.9939	0.9944
n-Hexane	0.9980	0.9951	0.9989	0.9972	0.9995
1.4-Dioxan	0.9977	0.9985	0.9992	0.9916	0.9909
Isopropyl acetate	0.9975	0.9962	0.9996	0.9956	0.9953
Pentanal	0.9966	0.9957	0.9991	0.9960	0.9941
n-Heptane	0.9969	0.9948	0.9996	0.9944	0.9927

[a] Isomers with identical mass contained in commercial gas mixture 1; no distinction possible as no individual substances available.

3.3 Robustness

The results from the variation of the sampling volume, the sampling flow rate, the relative humidity and the storage duration are displayed in Table 3 expressed by its impact on the recovery.

A significant influence of the variation of the sampling volume was observed for dichlorodifluoromethane and chloroethane at 1.6 L and for dichloroethane at 4 L: these very volatile compounds with boiling points of respectively 8.9, 12.3 and 40 °C will be breaking through the adsorbent bed in the sampling

Table 3 Robustness of the method for the 49 validated substances: influence of sampling volume, sampling flow rate, relative humidity and storage duration on the recovery of the compounds. All recoveries are calculated in comparison to a 0.8 L air sample taken at 80 mL min^{-1} at a relative humidity of 50% RH without storage

	Compared to 0.8 L		Compared to 80 mL min^{-1}		Compared to 50% RH		Compared to 0 d (tube storage)		
Substance	1,6 L, %	4 L, %	40 mL min^{-1}, %	120 mL min^{-1}, %	30, % RH	70, % RH	7 d, %	14 d, %	28 d, %
Dichlorodifluoromethane	10	7	114	31	94	37	113	61	90
Isobutane	108	111	94	94	98	95	111	93	83
1,3-Butadiene	106	105	95	94	98	94	108	95	84
Chloroethane	21	1	94	81	91	93	106	102	88
cis/*trans*-2-butene[a]	106	105	96	94	98	95	112	101	92
n-Butane	109	114	96	94	98	95	112	95	89
cis/*trans*-2-butene[a]	106	106	96	94	98	95	111	100	90
Acrolein	99	94	98	91	100	87	112	106	86
Furan	107	108	95	94	96	99	113	112	107
Propanal	100	97	100	97	98	75	103	102	65
Acetone	107	107	100	100	104	100	121	128	163
Dichloromethane	102	29	99	97	97	98	105	99	85
Acrylonitrile	104	95	99	100	100	101	107	99	91
Carbon disulfide	105	106	96	97	98	99	109	107	91
Isopropanol	100	95	101	101	112	99	97	114	104
Trichlorofluoromethane	99	96	93	91	96	97	107	114	108
1,1-Dichloroethene	105	106	96	95	99	100	107	106	100
Bromoethane	103	99	98	95	96	91	96	95	45
Methyl acetate	103	102	100	98	99	97	106	104	83
2-Chloropropane	97	91	94	91	95	96	104	110	89
1-Propanol	102	98	102	102	124	101	87	85	69
Diethyl ether	104	102	100	98	99	95	107	107	103
Isopentane	105	105	97	95	98	93	112	102	96
Propanenitrile	104	103	101	102	104	104	107	98	96
Isoprene	105	105	96	95	97	98	109	109	101
n-Pentane	106	105	96	95	98	94	112	95	89
tert-Butanol	101	99	100	102	115	104	86	87	73
Methacrolein	109	107	101	98	102	109	137	122	118
Cyclopentane	105	108	97	96	96	97	109	110	101
Isobutanal	94	94	101	101	94	76	56	65	31
Vinyl acetate	101	94	86	104	100	98	109	114	70
Methacrylonitrile	104	102	101	101	100	100	108	104	102
Chloroform	97	91	95	92	93	92	108	120	108
Butanal	104	103	99	97	99	93	104	111	69
Tetrahydrofuran	104	102	101	100	101	98	106	103	100
2-Butanone	105	103	102	100	103	99	109	115	97
Methyl acrylate	105	102	100	99	102	101	108	104	97
Ethyl acetate	105	102	100	98	100	99	108	107	102
1,2-Dichloroethane	105	103	101	100	104	102	104	97	87
Methyl *tert*-butyl ether	103	102	101	101	104	99	101	103	98
2-Methylpentane	104	104	98	98	99	98	107	107	102
Benzene	103	106	101	99	102	99	114	111	112
Tetrachloromethane	105	103	101	100	102	102	104	103	91
Trichloroethene	106	103	102	101	104	103	107	99	96
n-Hexane	104	103	98	96	97	94	111	103	96
1,4-Dioxane	106	103	104	104	112	108	102	94	95
Isopropyl acetate	105	102	101	99	103	100	105	102	99
Pentanal	105	102	102	99	105	98	98	92	58
n-Heptane	105	104	101	100	101	102	110	103	101

[a] Isomers with identical mass contained in commercial gas mixture 1; no distinction possible as no individual substances available.

tube. However, the volatility does not seem to be the only factor affecting the interaction of compounds with the adsorbent, as 1,3-butadiene (boiling point: −4.5 °C), butene (boiling point: 0.9 °C) or trichlorofluoromethane (boiling point: 23.7 °C) do not break through. Other possible explanations for the poor adsorption might be the polarity of the compounds but also steric effects, which could not be finally elucidated.

The variations of the sampling flow rate had a low influence, except for dichlorofluoromethane for which a breakthrough happened at 120 mL min^{-1}. Chloroethane had a similar behavior, but to a smaller extent.

In emission test chamber studies, the humidity is typically kept at 50% RH[3,15] but real indoor air samples can have higher and lower humidity levels. The recoveries of the alcohols isopropanol, 1-propanol and *tert*-butanol increased at lower humidity (30% RH). Indeed, they display better recoveries on the adsorbent as they interact with fewer water molecules from the air flow. Dichlorofluoromethane, acrolein, propanal, and isobutanal showed significant losses for the higher humidity (70% RH). It is possible that these polar hydrophilic substances either bind to the water molecules from the supply air or are displaced from the sorbent surface. Other polar substances, such as methyl acetate, propanenitrile and 1,4-dioxane stayed on the adsorbent, but they are less volatile.

The recovery of acetone and methacrolein increased during storage: acetone can be found as a blank in Carbograph 5TD, so this increase can most likely be explained that way. Methacrolein is not known to be a possible blank in the adsorbent and might be the result of ingress of contaminants from the lab air or a degradation reaction of other larger compounds with active sites in the adsorbent but this could not be verified. For a storage duration of 7 days, isobutanal displayed already consequent losses whereas 1-propanol and *tert*-butanol showed only minimal losses. The same results were obtained after 14 days of storage, except for dichlorodifluoromethane which had significantly decreased. After 28 days, losses were observed for most of the more polar substances such as propanal, bromoethane, butanal and pentanal. It cannot be excluded that such losses are the result of permeation through caps and/or seals of the sampling tubes. However, it is strongly recommended that the tubes should be analysed as soon as possible after sampling.

3.4 Limits of detection and quantification

For 35 substances, the limits of decision (LODE), detection (LOD), and quantification (LOQ) could be determined according to DIN 32645 (ref. 11) and are presented in Table 4. For 14 other substances, the limits determined according to the protocol described in Section 2.2.2. are shown in Table 5. These values are given as amounts on the tube (in ng) corresponding to a mass concentration in air in μg m^{-3}, when a sample volume of 1 L is considered. For the vast majority of compounds, the LOQ achieved is much lower than the corresponding guideline values. Only for acrolein, the LOQ determined considering a 1 L air sample (47 μg m^{-3}) is higher than the corresponding NIK value (14 μg m^{-3}). By considering higher air sample volumes, a lower LOQ can be reached but the influence of the sampling

Table 4 Decision (LODE), detection (LOD) and quantification (LOQ) limits determined following DIN 32645. For the 14 compounds, the determined decision limit was higher than that of Cal4; the detection and determination limits were then determined following other methods (see Table 5)

Substance	LODE (ng)	LOD (ng)	LOQ (ng)
Dichlorodifluoromethane	7.8	15.5	50.4
Isobutane	0.9	1.8	4.4
1,3-Butadiene	1.8	3.6	9.1
Chloroethane	1.3	2.7	6.7
cis/*trans*-2-butene*	1.6	3.2	7.9
n-Butane	2.3	4.6	12.2
cis/*trans*-2-butene*	1.5	3.0	7.6
Propanal	3.9	7.8	22.5
Acetone	1.6	3.2	9.6
Dichloromethane	0.9	1.8	4.5
Carbon disulfide	1.2	2.3	6.3
Trichlorofluoromethane	10.7	21.3	102.3
1,1-Dichloroethene	0.4	0.9	2.2
Bromoethane	1.1	2.1	5.3
2-Chloropropane	5.7	11.4	30.4
Diethyl ether	1.2	2.5	6.3
Isopentane	2.1	4.2	10.5
Isoprene	1.3	2.5	6.6
n-Pentane	1.2	2.4	6.0
tert-Butanol	1.7	3.4	9.4
Methacrolein	1.2	2.5	6.2
Cyclopentane	0.7	1.4	3.6
Methacrylonitrile	0.9	1.7	4.3
Chloroform	9.0	17.9	71.9
Methyl acrylate	0.9	1.8	4.7
1,2-Dichloroethane	0.4	0.8	2.1
Methyl *tert*-butyl ether	0.4	0.8	1.9
2-Methylpentane	0.8	1.6	4.0
Benzene	2.3	4.6	15.6
Tetrachloromethane	0.6	1.3	3.2
Trichloroethene	0.5	1.0	2.5
n-Hexane	1.6	3.3	8.1
Isopropyl acetate	1.1	2.3	5.7
Pentanal	1.2	2.4	6.2
n-Heptane	1.4	2.7	7.2

Table 5 Detection (LOD) and determination (LOQ) limits of the 14 substances for which DIN 32645 was not applied. The LOD and LOQ_1 are determined according to[12] as presented in 2.2.2., while the LOQ_2 was the lowest calibration level Cal*n* for which the coefficient of determination of the calibration Cal1–Cal*n* was higher than 0.99

Substance	LOD (ng)	LOQ_1 (ng)	LOQ_2 (Cal $R^2 > 0.99$)
Acrolein	0.25	0.82	Cal8: 47 ng
Furan	0.15	0.50	Cal7: 11 ng
Acrylonitrile	0.13	0.44	Cal7: 8.8 ng
Isopropanol	0.34	1.12	Cal8: 21 ng
Methyl acetate	0.11	0.38	Cal7: 21 ng
1-Propanol	1.08	3.60	Cal8: 54 ng
Propanenitrile	0.15	0.50	Cal7: 11 ng
Isobutanal	0.23	0.75	Cal7: 11 ng
Vinyl acetate	0.33	1.10	Cal7: 18 ng
Butanal	0.54	1.81	Cal7: 13 ng
Tetrahydrofuran	0.06	0.19	Cal7: 11 ng
2-Butanone	0.26	0.85	Cal7: 12 ng
Ethyl acetate	0.51	1.69	Cal7: 16 ng
1,4-Dioxane	0.14	0.48	Cal9: 31 ng

volume on the result should be checked (see Section 3.3. and Table 3). As a low influence of the sampling volume was obtained for acrolein in our study, a LOQ of 12 μg m^{-3} can be reached, when a 4 L sample is taken. A previous study which considered a 4 L air sample reached a lower LOQ of 2 μg m^{-3} but was focused on this single compound.[9] For the other common compounds, the LOQs achieved by considering a 4 L sample are in the same range as in the validation from Schieweck *et al.* (2018) in dry nitrogen.[8]

The analytical method presented here was optimized for a very broad range of substances. Taking into account fewer analytes, especially of a specific compound group, a further optimization of the method could lead to a further reduction of the LOD/LOQ.

3.5 Measurement uncertainty

The results of the combined measurement uncertainty at calibration level Cal 9 are displayed in Table 6. The details of the

Table 6 Combined measurement uncertainty of the method for the 49 validated substances at Cal9

Compound	$u(c_{GCT})/c_{GCT}$	u(tube spiking)	$u(cal)/m_{calculated}$	$u(prec)/m_{calculated}$	k	$u(m_{calculated})/m_{calculated}$
Dichlorodifluoromethane	14%	1%	8%	42%	2	91%
Isobutane	4%	1%	1%	12%	2	26%
1,3-Butadiene	3%	1%	1%	12%	2	26%
Chloroethane	12%	1%	5%	11%	2	35%
cis/*trans*-2-Butene[a]	4%	1%	1%	12%	2	25%
n-Butane	4%	1%	1%	13%	2	28%
cis/*trans*-2-Butene[a]	4%	1%	1%	12%	2	25%
Acrolein	5%	1%	1%	9%	2	20%
Furan	8%	1%	4%	7%	2	23%
Propanal	13%	1%	3%	7%	2	30%
Acetone	8%	1%	5%	6%	2	23%
Dichloromethane	5%	1%	5%	7%	2	19%
Acrylonitrile	7%	1%	4%	6%	2	21%
Carbon disulfide	7%	1%	5%	8%	2	24%
Isopropanol	8%	1%	5%	8%	2	25%
Trichlorofluoromethane	13%	1%	2%	8%	2	31%
1,1-Dichloroethene	7%	1%	4%	8%	2	23%
Bromoethane	7%	1%	3%	7%	2	21%
Methyl acetate	7%	1%	4%	6%	2	21%
2-Chloropropane	12%	1%	1%	10%	2	31%
1-Propanol	9%	1%	5%	8%	2	27%
Diethyl ether	9%	1%	4%	7%	2	24%
Isopentane	5%	1%	1%	11%	2	24%
Propanenitrile	10%	1%	4%	6%	2	25%
Isoprene	2%	1%	4%	8%	2	18%
n-Pentane	5%	1%	1%	12%	2	26%
tert-Butanol	9%	1%	4%	8%	2	25%
Methacrolein	7%	1%	6%	5%	2	21%
Cyclopentane	4%	1%	3%	8%	2	18%
Vinyl acetate	7%	1%	3%	15%	2	33%
Methacrylonitrile	8%	1%	4%	6%	2	21%
Chloroform	13%	1%	2%	8%	2	30%
Butanal	4%	1%	6%	7%	2	20%
Tetrahydrofuran	11%	1%	4%	5%	2	26%
2-Butanone	8%	1%	5%	6%	2	23%
Ethyl acetate	7%	1%	4%	5%	2	20%
1,2-Dichloroethane	7%	1%	5%	5%	2	20%
Methyl tert-butyl ether	8%	1%	4%	5%	2	21%
2-Methylpentane	5%	1%	3%	8%	2	20%
Benzene	8%	1%	5%	5%	2	22%
Tetrachloromethane	6%	1%	3%	5%	2	17%
Trichloroethene	6%	1%	5%	4%	2	18%
n-Hexane	6%	1%	1%	9%	2	22%
1,4-Dioxan	10%	1%	6%	6%	2	26%
Isopropyl acetate	5%	1%	4%	5%	2	17%
Pentanal	35%	1%	5%	6%	2	73%

[a] Isomers with identical mass contained in commercial gas mixture 1; no distinction possible as no individual substances available.

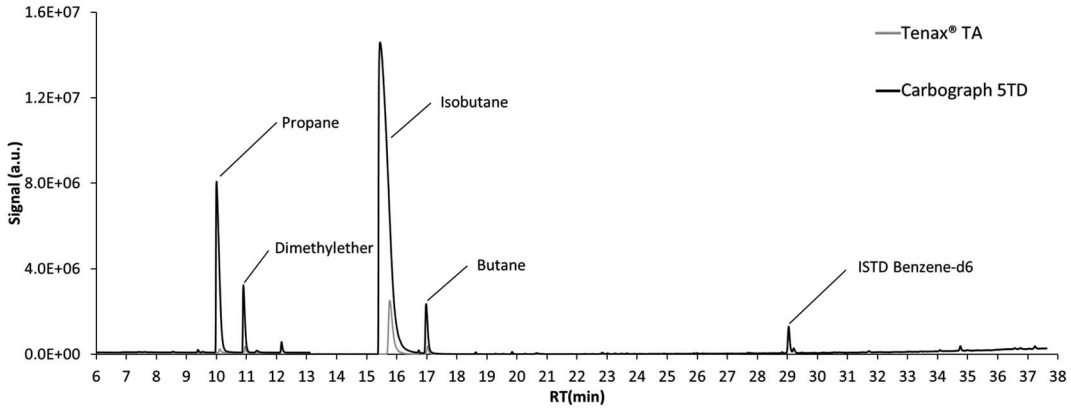

Fig. 2 Chromatogram of the emissions of the polyurethane foam after 7 days in the emission test chamber.

calculation are given in ESI Table S4.† It was not calculated for isobutanal and methyl acrylate because the gas standards could not be prepared for a third repetition due to a lack of chemicals. For heptane, the results are not displayed because it was present in every solution, which make the calculation very complex. It did furthermore not belong to the target substances. Two compounds had uncertainties above 35%: dichlorodifluoromethane (91%) and pentanal (73%). For dichlorodifluoromethane, high deviations of the GC/MS signal over several repetitions were observed, which shows poor precision for this compound. As these deviations appear three times in the calculation (see Section 2.2.4.), the real measurement uncertainty might probably be lower but cannot be reliably determined here. For pentanal, the high value from the measurement uncertainty is caused by the high standard deviation from the preparation of the standards (34%): as the solutions were prepared in three different years and the pentanal signal decreased, pentanal is probably unstable in the solution of group 5. All the other substances had uncertainties below 35%, which is satisfactory for such volatile compounds.

3.6 Example of an emission test chamber measurement

The chromatogram of the air sampled from the emission test chambers on day 7 after loading of the polyurethane foam is displayed in Fig. 2. Propene, dimethyl ether, isobutane and butane displayed high signals. For all these compounds, the signals resulting from the same air volume sampled on Tenax® TA were much lower than those on Carbograph 5TD, while the signal of ISTD benzene-d_6 was constant. This demonstrates again the low suitability of Tenax® TA for sampling VVOCs, as shown in previous studies.[5,6] As propene and dimethyl ether could not be validated in this study and the isobutane signal was above the calibration range used during validation, butane was chosen as an example for quantification.

While considering an uncertainty based only on the standard deviation from 3 air samples, the butane air concentration in the emission test chamber was 155.4 ± 2.7 μg m^{-3}. For the calculation of the combined uncertainty, the uncertainty of the sampling pump (5%) was added here, and the result of the quantification is then 155 ± 46 μg m^{-3}. This shows the importance of the consideration of measurement uncertainty for VVOC air analysis.

4 Conclusions

This work presents a thorough study of the capability of Carbograph 5TD for VVOC analysis. The main progress lies in the consideration of a wide range of compounds and the study of the influence of different parameters on the performance of the method. Satisfactory recoveries (above 70%) and calibrations were achieved for 49 compounds (36 VVOCs) considering different spiking modes. The most volatile and polar substances are sometimes vulnerable to changes in the parameters: they can display losses at a high sampling volume, high relative humidity or longer storage duration. Dichlorofluoromethane has satisfactory recoveries, but the method is not robust for this analyte. LOQs in indoor air or emission guideline values and combined measurement uncertainties under 35% can be achieved with this approach. To extend the capacities of the method to the whole VVOC range, Carbograph 5TD should be combined with a stronger hydrophilic adsorbent but a reliable method for water management is still needed.

Author contributions

Morgane Even: conceptualization, methodology, validation, formal analysis, investigation, data curation, writing – original draft preparation, visualization, project administration. Elevtheria Juritsch: conceptualization, methodology, validation, formal analysis, investigation, writing – reviewing and editing. Matthias Richter: conceptualization, writing – reviewing and editing, supervision, project administration, funding acquisition.

Conflicts of interest

There are no conflicts of interest to declare.

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