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Supplement of

Preparation and analysis of zero gases for the measurement of trace VOCs in air monitoring

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1 Analytical systems

Table S1. Specifications of the analytical systems used to test the purification systems.

	DWD OVOC GC	DWD Biogenic VOC GC**	DWD NMHC GC* + **	VSL GC	INRIM GC***
Analytes	OVOCs (C ₁ -C ₄), acetonitrile	Monoterpenes and heavier VOCs (C ₅ -C ₁₄)	NHMCs and aromatics (C ₂ -C ₈)	NMHCs and aromatics (C ₂ -C ₉)	OVOCs: methanol, ethanol, acetone
Sampling system	On-line, custom-made sampling unit	On-line, custom-made sampling unit	On-line, custom-made sampling unit with Sample Preconcentration Trap (SPT)	On-line, thermal desorber series 2 UNITY-Air Server / CIA 8 from MARKES International (UK)	On-line, SPT
O₃ destruction	Ozone was destructed by the palladium catalyst used for the generation of the in-house zero air for the tests			No problems with ozone and water as the in-house zero gas used for the tests came from synthetic air cylinder	
H₂O management	Cold trap: 1/8" (ID 2.1 mm) Silcosteel [®] (Restek) tube, 16 cm cooled length, -30°C, reconditioning at 130°C between runs	Dry purge of the adsorption trap with helium, 750 ml at 30°C	Cold trap: 1/8" (ID 2.1 mm) Sulfinert [®] (Restek) tube, 50 cm cooled length, -45°C, reconditioning at 100°C between runs		
VOC trap	1/8" Sulfinert tube filled with Carbopack B, Carbopack X and Carbosieve SIII	Fritted glass tube filled with Tenax TA, Carbopack X and Carboxen 569	cryo-adsorption on glass beads (SPT, Varian)	MARKES Ozone Precursors/Freon trap (U-T5O3F-2S)	cryo-adsorption on glass beads (SPT, Bruker)
Trap temperatures	0°C/200°C	30°C/200°C	-180°C/130°C	-30°C/300°C	-50°C/200°C
Sample volume [ml]	675 ml	1500 ml	750 ml	900 ml	3200 ml
Refocus and temperatures	No refocus	Cryogenic refocusing in a fused silica capillary, -180°C/ 60°C	No refocus		
GC model	Agilent 7890A	Agilent 6890	Varian CP-3800	Trace GC Ultra (Inter Science FINNIGAN)	Bruker 450
GC column(s)	PoraBOND U (Agilent) PLOT, 25 m x 0.32 mm x 7 µm	BPX-5 (SGE), 50m x 0.22 mm x 1 µm	Al ₂ O ₃ (KCl-passivated) PLOT (Varian), 50 m x 0.53 mm	Deans switch: GS-Alumina PLOT (Agilent), 50 m x 0.53 mm and CP-WAX 52	PoraBOND U (Agilent) PLOT, 25 m x 0.32 mm x 7 µm

				CB (Agilent), 60 m x 0.32 mm x 0.25 μ m	
Carrier gas	Helium 5.0 cleaned with charcoal cartridge			Helium 6.0	Helium 6.0
Detectors	FID and MS (electron impact ionisation and quadrupole detector), split after the GC column to both detectors		FID	2 FIDs, one for each GC column	FID
Calibration	Reference gas standard from AiR [®] (Apel-Riemer Environmental Incorporated, USA), 100-250 nmol/mol	Reference gas standard from NPL (National Physical Laboratory, United Kingdom), 2 nmol/mol		Dynamic dilution of a gravimetric primary gas mixture prepared by VSL	Dynamic dilution of a dynamic primary gas mixture, prepared by diffusion according to ISO 6145-8 by INRIM
VOC mixture used for the tests	Dilution of an OVOC mixture by NPL (5 μ mol/mol)	Dilution of an NMHC + monoterpene mixture by NPL (100 nmol/mol)			
Limit of detection	10 – 30 pmol/mol	\leq 2 – 5 pmol/mol	\leq 3 – 10 pmol/mol	2-15 pmol/mol	3 – 11 pmol/mol

*Plass-Dülmer et al. (2002), ** Hoerger et al. (2015), *** Demichelis et al. (2016)

2 Data analysis methods for zero gas characterization

2.1 Quantification of VOC impurities in zero gases and handling of system internal blanks

The quantification of zero gas impurities x_{imp} is given by

$$x_{\text{imp}} = (y - B)/A \quad (1)$$

- 5 where y is the measured signal of the investigated impurity [$\mu\text{V min}$] and B is the signal of the system internal blank [$\mu\text{V min}$]. The signals are defined by the integration of the detector response [μV] in the identified retention time interval [min] of the investigated VOC, i.e. the VOC peak area. A is the detector sensitivity to the investigated VOC [$\mu\text{V min} / \text{concentration}$], the so-called calibration factor.

- 10 Identification of internal blanks B , i.e. system artefacts, and discrimination of them from zero gas impurities is done by measuring different sample volumes in step 1 of the measurement procedure (Sect. 2.2). A proportional relationship of the detector response with the sampled volume is expected for impurities in the zero gas measured, whereas for GC system internal blanks the detector response is expected to be independent of the sample volume.

2.2 Determination of the analytical detection limit

- 15 Gas chromatography measurements at very low concentrations like in this study demand low limits of detection. The detection capability, i.e. detection limit x_D is defined by IUPAC as the smallest measure that can be detected with reasonable certainty for a given analytical procedure. Other definitions of the limit of detection are reported in literature (Belter, 2014) and different approaches based on regression of gas standards are described (Shrivastava, 2011, Belter, 2014, IUPAC, 1995).

- 20 Following IUPAC, the detection limit is based on Neyman–Pearson theory of hypothesis testing (IUPAC, 1995). This definition considers the probability of false positive α and false negative β detections and focuses on reducing the probabilities of making errors. The correctness of the method was proved by Voigtman (2008). x_D is calculated by Currie's formula Eq. (2) (IUPAC, 1995), where a linear calibration curve is assumed and the detector signal y is described by $y = B + Ax$, with the regression intercept B (blank value), the sensitivity A (calibration factor) and the analyte amount x .

$$x_D = \frac{2 t_{1-\alpha, \nu} \sigma_0 K}{A I} \quad (2)$$

with

$$25 \quad K = 1 + r(A, B) \frac{u(B) t_{1-\alpha, \nu} u(A)}{\sigma_0 A} \quad (3)$$

$$I = 1 - \left[t_{1-\alpha, \nu} \frac{u(A)}{BA} \right]^2 \quad (4)$$

$$r(A, B) = -\frac{\bar{x}}{x_q} \quad (5)$$

where σ_0 is the standard deviation of the measured system internal blank. If no internal blank is present, the standard deviation of the baseline signal is used. This value is experimentally assessed by integrating the noise of the detector over a time interval similar to the average peak width for a serial of zero gas measurements. $t_{1-\alpha, \nu}$ is the t-student value for ν degree-of-freedom (equal to $n-2$) and α level of significance (equal to 0.05 – one tail). $r(A, B)$ is the correlation coefficient with \bar{x} as the mean of the n samples and x_q as the quadratic mean. $u(A)$ and $u(B)$ are the uncertainties of the calibration factor and blank value, respectively. If the uncertainties of the linear calibration function parameters are negligible (IUPAC, 1995, Sect. 3.7.5.1), $\frac{K}{I} \approx 1$, equation 2 simplifies and the detection limit x_D is calculated by:

$$x_D = k \cdot \sigma_0 / A \quad (6)$$

10 where $k = 3.29$ and A is the calibration factor.

To improve the detection limit of a GC device several parameters can be optimised summarised in Table 1.

Table S2. Opportunities for detection limit x_D improvement of GC measurement systems.

Opportunities for x_D improvement	Description	Actions
$\downarrow \sigma_0$ (when system internal blanks are detected)	Improve reproducibility of system internal blank measurements Improve baseline noise	- realize reproducible system cleaning - realize reproducible pre-concentration - employ high purity carrier gas and detector gases
$\uparrow A$	Increase detector sensitivity Increase the amount of compound reaching the detector and/or in the case of FID the ion production rate in the flame	- increase sampled mass (or volume) on the VOC trap - increase the mass flow rate ratio hydrogen/air, the makeup mass flow rate (prefer N_2 to He), the FID temperature
$\downarrow t_{1-\alpha, \nu}$	Increase ν degree-of-freedom	- increase N (number of blank determinations)
$\downarrow u_A$ and u_B	Improve regression quality	- design a suitable regression experiment in terms of number of gas standards and gas standards range (for non-linear detectors)

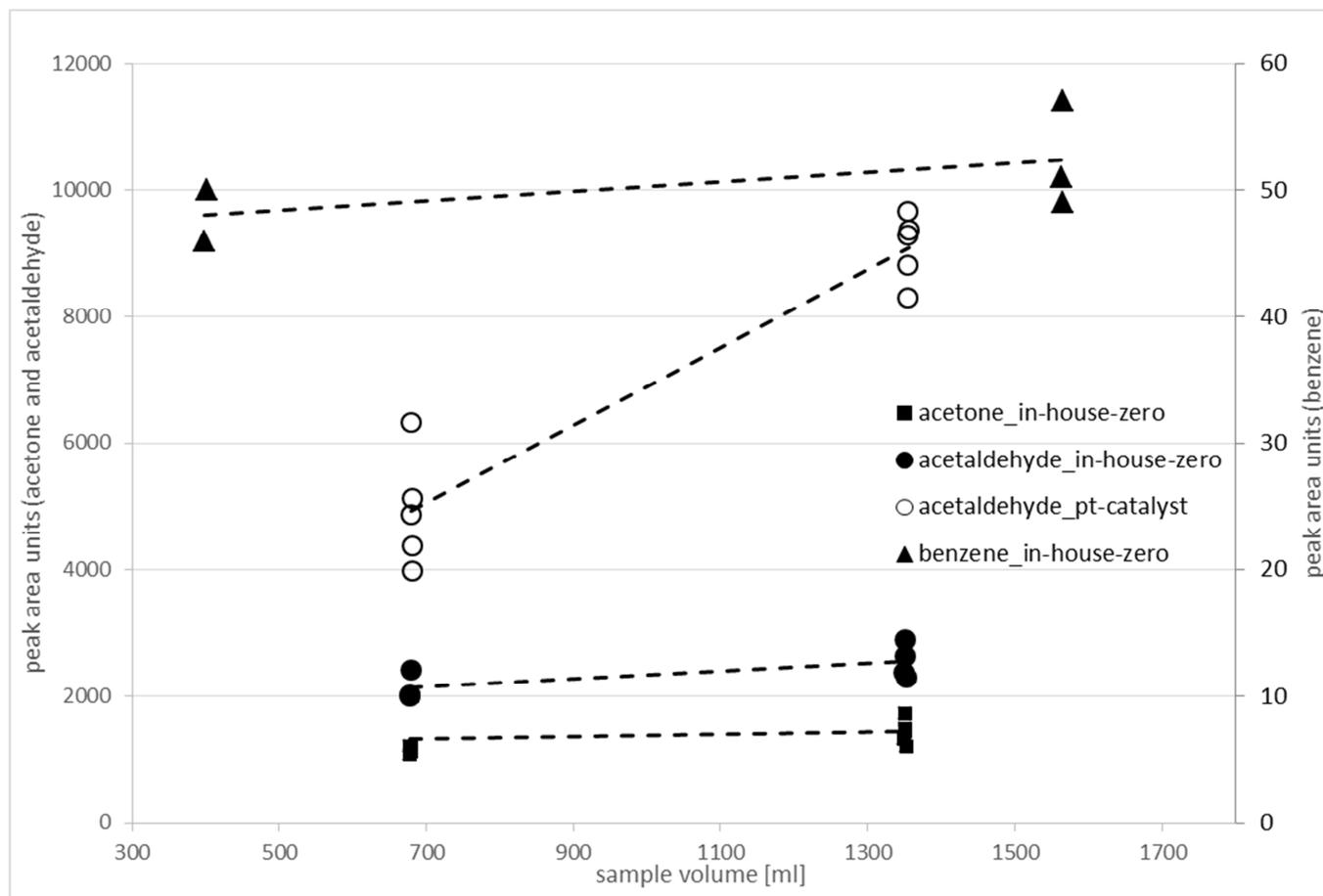
Table S3 contains the detection limits x_D for the various tested VOCs calculated with the method of IUPAC (IUPAC, 1995).

Table S3. Tested VOCs by lab with the individual detection limits in pmol/mol.

	compound	DWD	VSL	INRIM
NMHCs	ethane	3	20	
	ethene	7	21	
	propane	2	10	
	propene	3	11	
	isobutane	1	10	
	ethyne	10	15	
	n-butane	1	11	
	trans-2-butene	1	4	
	1-butene	2	4	
	isobutene		6	
	cis-2-butene	1	3	
	isopentane	1	3	
	n-pentane	1	8	
	1,3-butadiene	1	5	
	trans-2-pentene	1	13	
	1-pentene	1	3	
	2-methylpentane	1	6	
	n-hexane	1	1	
	isoprene	2	4	
	n-heptane	1	4	
	benzene	2	3	
	2-2-4-trimethylpentane	1	4	
	n-octane	1	5	
toluene	6	4		
ethylbenzene	5	7		
p-, m-, o-xylene	5	6		
1-3-5-trimethylbenzene	6	10		
1-2-4-trimethylbenzene	2	16		
1-2-3-trimethylbenzene	2			
monoterpenes	alpha-pinene	4		
	myrcene	3		
	3-carene	2		
	cis-ocimene	2		
	p-cymene	2		
	limonene	2		
	camphor	2		
	1,8-cineole	5		
OVOCs	methanol	77	110	3
	acetaldehyde	84	110	
	ethanol	26	120	11
	acetone	31	80	11
	MEK	2	180	
	methacrolein		110	
acetonitrile	-	6		

3 Analysis of internal blanks

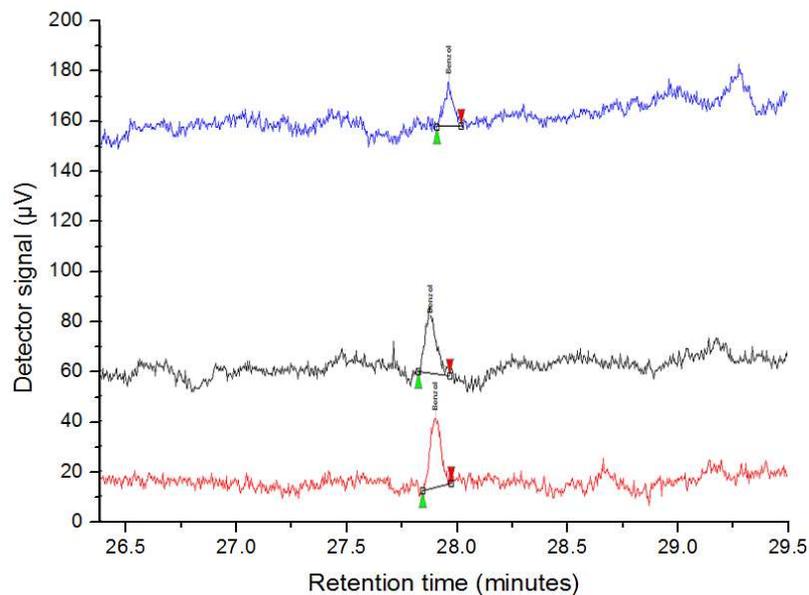
In order to distinguish between internal blanks and impurities of the in-house zero air, zero air was sampled at two different sample volumes. In Figure S1, peak areas measured in DWD in-house zero air at different sample volume are shown for benzene, acetone and acetaldehyde. While benzene was measured by DWD's NMHC GC (Table S1), acetone and acetaldehyde were analysed with DWD's OVOC GC. All three compounds exhibit characteristics of an internal blank and are independent of the sample volume for directly measured samples of the in-house zero air. A different behavior was observed for acetaldehyde while flushing in-house zero air through the platinum catalyst at an early stage of usage. In the case the peak area was strongly affected by the sample volume.



10 **Figure S1.** Peak areas for benzene, acetaldehyde and acetone observed at two different sample volumes: 1590ml and 390ml for benzene and 680ml and 1350ml for acetaldehyde and acetone. All peaks observed in the directly measured in-house zero air (filled symbols) are independent of the sample volume. For acetaldehyde however, peaks observed in samples of in-house

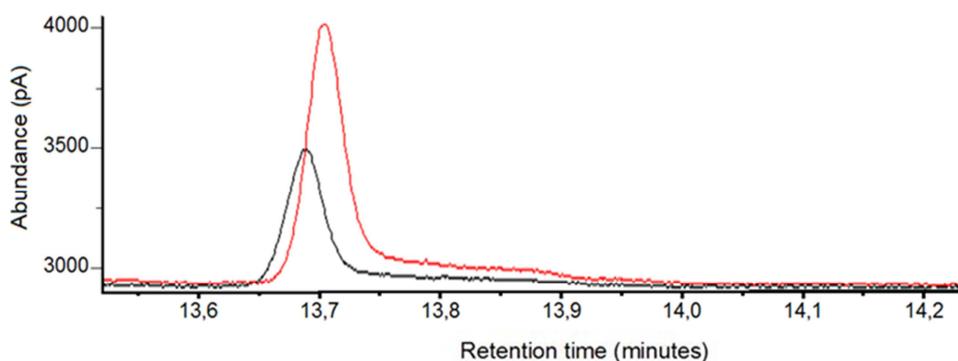
zero gas which was flushed through the platinum catalyst at an early stage of usage (empty circles) are strongly affected by the sample volume.

Figure S2 and S3 show example chromatograms of the DWD GC systems recorded at different sample volumes for benzene and acetaldehyde, respectively.



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Figure S2. Example chromatograms for a GC internal blank of benzene (peak in flame ionisation detector signals at the retention time of benzene). Measurements of zero gas at different sample volumes: 300 ml (blue); 800 ml (black) and 1400 ml (red). The benzene peak area is independent of the sample volume.



10 **Figure S3.** Example chromatograms for an impurity released by the platinum catalyst at an early stage of operation. Measurements of zero gas at two sample-volumes: 680 ml (black) and 1360 ml (red). There is a proportional relationship of

the detector response with the sample volume of air leaving the purifier. In the example the acetaldehyde impurity concentration was about 300 pmol/mol.

4 Results and discussion

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Figures S4 and S5 show example chromatograms for measurement steps (1-3; Section 2.2 main paper) performed with catalytic purifying (S4) and the adsorption cartridge (S5).

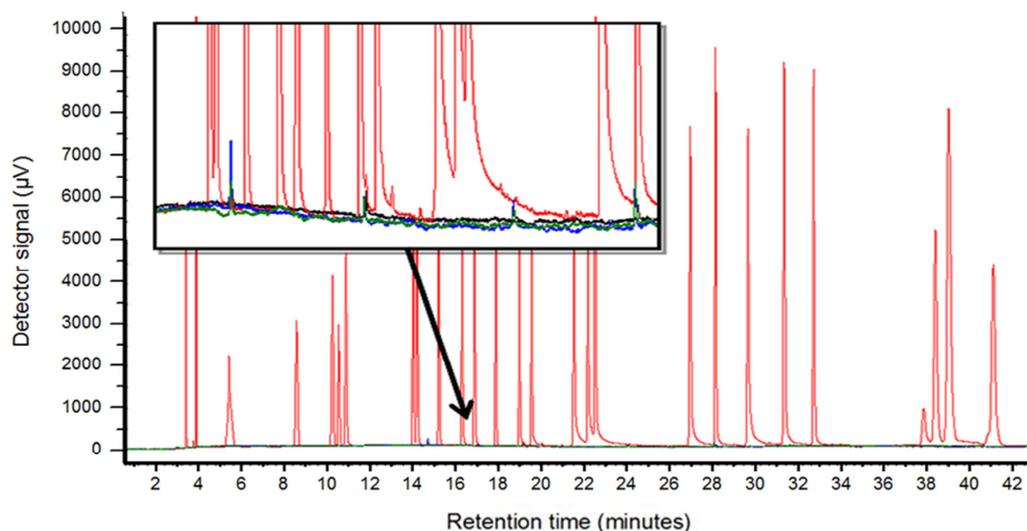


Figure S4. Example for the results of the catalysts, in this case the catalyst with platinum on aluminium oxide pellets (GC chromatograms): Zero gas (black), zero gas passing the catalyst (blue) confirming no relevant additional impurities are introduced by this catalyst, 1.2 nmol/mol mixture of different NMHCs (red) and the same mixture leaving the catalyst (green). Four small peaks below 10 pmol/mol are the result of system internal blanks (the same peaks are present in the measurements of zero gas). All these measurements were conducted with the same sample volume.

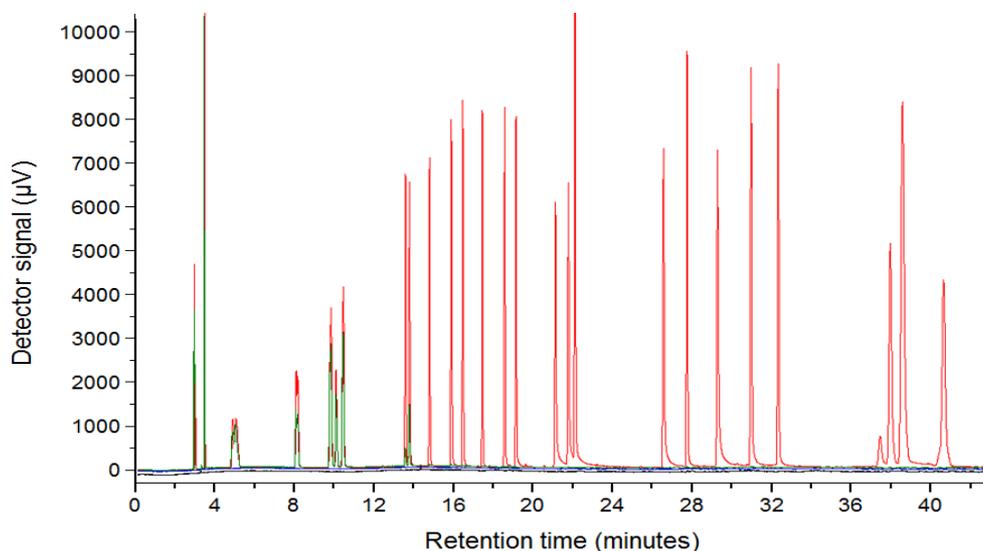


Figure S5. Example for the breakthrough of the light NMHCs C₂ to C₄ through the adsorption cartridge (GC chromatograms): 1.2 nmol/mol mixture of different NMHCs (red) and the same mixture leaving the catalyst (green) with a breakthrough of the light NMHCs (up to minute 14) being almost as high as the input. All these measurements were conducted with the same sample volume.

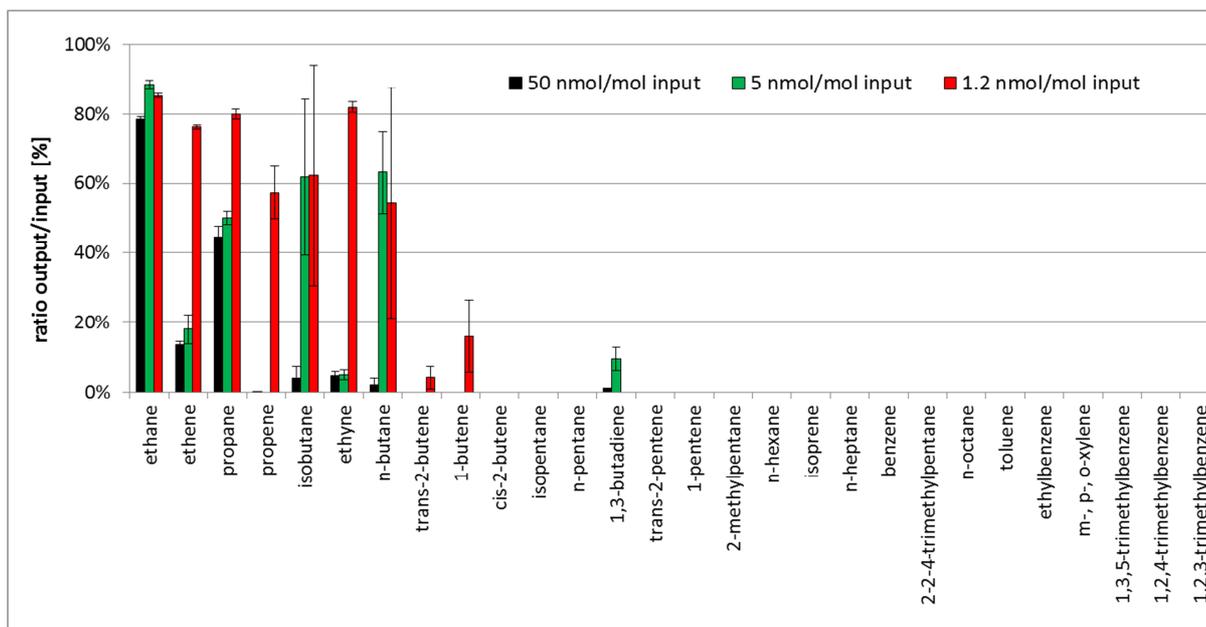


Figure S6. Results of the adsorption cartridge (ratios output/input) for an input of 50 nmol/mol (black), 5 nmol/mol (green) and 1.2 nmol/mol NMHCs (red). Error bars indicate the standard deviations of 5 measurements.

In Figure S6, the average output-to-input ratio for different input mole fractions and substances is shown. A ratio of 0% implies that the purifier removes the substance efficiently, whereas a ratio of 100% denotes a complete breakthrough of a substance. Except for ethane, the removal efficiency is not consistent for different input concentrations. For ethene, propane, propene, ethyne, trans-2-butene and 1-butene the 1.2 nmol/mol input was less efficiently purified compared to the higher inputs.

In Figure S7, the results of the measurement series for 50 nmol/mol and 5 nmol/mol input are plotted for isobutane and n-butane. For the 50 nmol/mol input the output is increasing from measurement to measurement, while the reverse behaviour is observed for the 5 nmol/mol input. The latter measurements were conducted directly after the high input of 50 nmol/mol and most likely memory effects occurred. This means after supplying high VOC amounts to the cartridge, some VOCs are released by the cartridge even if the input level is reduced again.

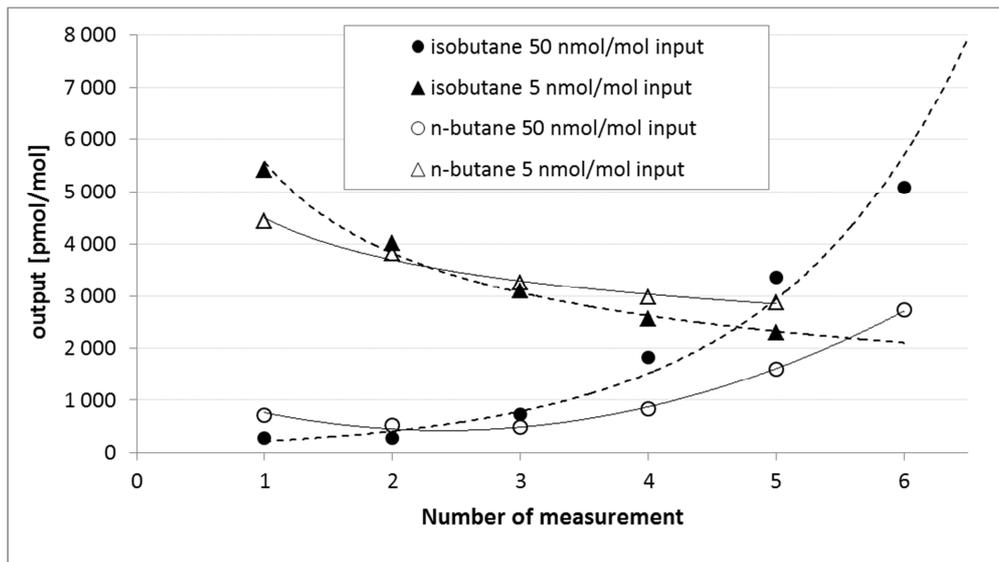


Figure S7. Adsorption cartridge breakthrough of isobutane and n-butane increasing with the runtime of the 50 nmol/mol mixture. A memory effect of the purifier was observed in the following measurements with 5 nmol/mol input.

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15