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Supplementary Information (SI)

DETERMINATION OF ACROLEIN IN AMBIENT AIR AND IN THE ATMOSPHERE OF ENVIRONMENTAL TEST CHAMBERS

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S1. Calibration

An aliquot of 1 µL of the liquid standard solution (acrolein in methanol, 1 mg mL^{-1}) was injected on Carbograph 5TD tubes. n=10 equidistant calibration points x_i (1:10 – 1:10000) and m=3 samples of each concentration x_{01} to x_{10} were measured (see Table S1). A low concentration range from 0.01 mg mL^{-1} to 0.001 mg mL^{-1} and a high concentration range from 0.1 mg mL^{-1} to 0.002 mg mL^{-1} were defined. Lower concentrations were not considered as obtained peak areas were in the range of the tube blank value. The limit of detection (LOD) and the limit of quantitation (LOQ) were calculated from the linear calibration curve $y = a \cdot x + b$ based on the approach given by Einax et al.[1] and in accordance with DIN 32645.[2]

For an analytical uncertainty of 33.3%, a significance level of 95% ($\alpha = 0.05$) and a sampling volume of 4 L, a LOD of 0.1 µg m^{-3} and a LOQ of 0.4 µg m^{-3} were calculated for the low concentration range ($7.86 \cdot 10^{-3}$ mg mL^{-1} – $7.86 \cdot 10^{-4}$ mg mL^{-1}). For the high concentration range ($7.86 \cdot 10^{-2}$ mg mL^{-1} – $1.57 \cdot 10^{-3}$ mg mL^{-1}) a LOD of 0.2 µg m^{-3} and a LOQ of 0.8 µg m^{-3} were obtained. A higher sampling volume lowers LOD and LOQ, but requires longer collection times. For the sampling of 6 L the following limits can be calculated: 0.08 µg m^{-3} (LOD) and 0.3 µg m^{-3} (LOQ) for the low concentration range; 0.1 µg m^{-3} (LOD) and 0.5 µg m^{-3} (LOQ) for the high concentration range. Figure S1 shows the calibration data and linear regression curves for both ranges. If a mixture of several VVOCs is used as standard solution, the obtained LOD and LOQ might differ due to higher blanks.

Calculation of the limit of detection x_{LOD}:

$$x_{LOD} = s_{x0} \cdot t_{f;\alpha} \sqrt{\frac{1}{m} + \frac{1}{n} + \frac{\bar{x}^2}{Q_x}} \tag{S1}$$

s_{x0} is the standard deviation of the method, $t_{f;\alpha}$ is the t-value for *f* degrees of freedom and an error probability *α*, *k* is a conventional factor to weight the uncertainty of the result and is usually set to *k* = 3 for an uncertainty of 33.3% and a significance level of 99% (*α = 0.01*). *n* is the number of calibration points x_i, *m* is the number of samples measured of each concentration $x_n - x_{n+1}$. $\bar{x}^2$ is the square of the arithmetic mean of the content of all calibration samples and Q_x is the sum of quadratic deviations of *x*.

Calculation of the limit of quantitation x_{LOQ}:

$$x_{LOQ} = k \cdot s_{x0}\, t_{f,\alpha} \sqrt{\frac{1}{m} + \frac{1}{n} + \frac{(x_{LOQ} - \bar{x})^2}{Q_x}} \tag{S2}$$

Eq. (S2) is recursive starting with $x_{LOQ} = k \cdot x_{LOD}$. The standard deviation of the method s_{x0} is calculated from Eq. (S3).

$$s_{x0} = \frac{s_{y,x}}{b} \tag{S3}$$

$s_{y,x}$ is the residual standard deviation of the calibration measurement values and *b* is the slope of the linear calibration curve.

Table S1: Dilution stages (n=10 equidistant calibration points x_i), corresponding concentrations (mg mL^{-1}), peak areas and measured standard deviations (SD).

Dilution	**Concentration [mg mL^{-1}]**	**Area [A]**	**Standard deviation (SD)**
1:10	0.0786	4192833	87302
1:20	0.0393	2221298	35194
1:50	0.01572	900089	27963
1:100	0.00786	534599	16370
1:200	0.00393	303366	20825
1:500	0.001572	189732	11793
1:1000	7.86E-4	169688	21766
1:2000	3.93E-4	166852	6636
1:5000	1.572E-4	143063	21342
1:10000	7.86E-5	127898	18915

Table S2: Concentration ranges, limits of detection (LOD) and limits of quantitation (LOQ) for certain statistical conditions and corresponding calibration data.

Range		**Low concentration**		**High concentration**	
Dilution		1:100 - 1:1000		1:10 - 1:500	
Concentration [mg mL^{-1}]		0.00786 - 0.000786		0.0786 - 0.001572	
k	**α**	**LOD 1) [µg m^{-3}]**	**LOQ 1) [µg m^{-3}]**	**LOD 1) [µg m^{-3}]**	**LOQ 1) [µg m^{-3}]**
3 (33.33%)	0.01 (99%)	0.2	0.8	0.3	1.2
3 (33.33%)	0.05 (95%)	0.1	0.4	0.2	0.8
Calibration data					
Calibration: y = a + b * x					
a		113,492 ± 14,159		110,892 ± 19,884	
b		5.26E7 ± 3.2E7		5.23E7 ± 5.43E6	
Pearson's R		0.9928		0.9996	

1) calculated for a sampling volume of 4 L.

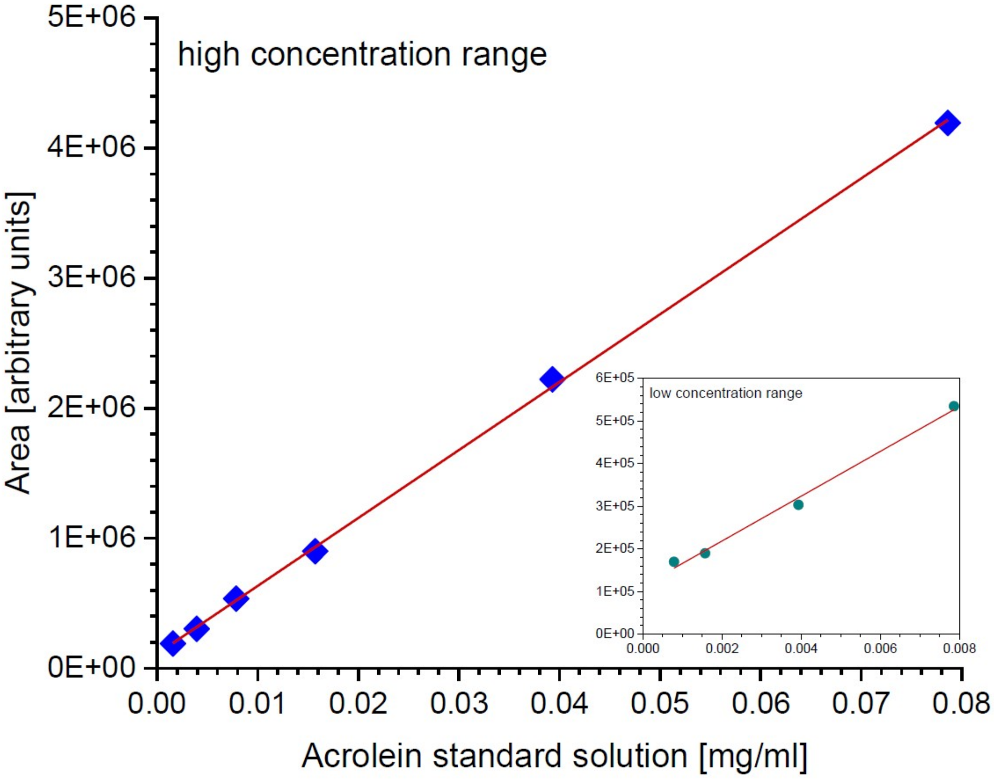

Figure S1. Calibration data and linear regression curves for the high concentration range and low concentration range (inset) of the acrolein standard.

S2. Breakthrough

For determining the breakthrough and the sampling reproducibility, two sampling tubes filled with Carbograph 5TD were connected in series. The first tube was spiked with an aliquot of 1 μL of the liquid analytical grade standard. The exit of the back-up tube was connected with a calibrated sampling pump. In total, ten tube pairs were sampled with a flow rate of 125 mL min^{-1} at a total sampling volume of 4 L. The breakthrough was calculated as percentage of acrolein found in the second tube in relation to the sum detected in the first and in the second sampling tube.

The breakthrough varied between 0.36% and 0.49% with an arithmetic mean of 0.43% and a standard deviation of 0.04%, which demonstrates the good sampling reproducibility. As a breakthrough of <5% is recommended at a specific sample volume,[3] an adjustment of the sample volume was not necessary.

S3. Settings of the PTR-QMS

$$[RH^+]_{ppb} = \frac{[RH^+]_{cps} \cdot 10^9 \cdot 1013.25 \cdot 22400 \cdot (273.15 + T_d) \cdot Tr_{H_3O^+}}{k_{acrolein} \cdot t_R \cdot [H_3O^+]_{cps} \cdot 6.022 \cdot 10^{23} \cdot 273.15 \cdot Tr_{RH^+}}$$

Table S3: Settings of the PTR-QMS.

T_d	60 °C
p_d	2.03 mbar
t_R	95 µs
Transmission coefficient Tr_{RH^+} (m/z 57)	0.832
Transmission coefficient $Tr_{H_3O^+}$ (m/z 21)	0.480
Transmission coefficient $Tr_{H_3O^+}$ (m/z 37)	0.577
Mass multiplier (m/z 57)	1
Mass multiplier (m/z 21)	500
Mass multiplier (m/z 37)	1
$k_{acrolein}$ (VOC default value)	$2.00 \cdot 10^{-9}$ cm³ s⁻¹
$k_{acrolein}$ (Zhao and Zhang)[4]	$3.35 \cdot 10^{-9}$ cm³ s⁻¹
$k_{acrolein}$ (Cappellin et al.)[5] (calculated for different settings of the PTR-MS)	$3.20 \cdot 10^{-9}$ cm³ s⁻¹ - $3.85 \cdot 10^{-9}$ cm³ s⁻¹
$k_{acrolein}$ (measured)	$2.95 \cdot 10^{-9}$ cm³ s⁻¹
M (acrolein)	56.06 g mol⁻¹

Conversion from ppb to µg m⁻³:

$$1\ \mu g/m^3 = 1\ ppb \cdot \frac{M}{22.40 \cdot \frac{T}{273.15} \cdot \frac{1013.25}{p}}$$

M is the molecular weight in g mol^{-1}, T is the temperature in K and p is the atmospheric pressure in hPa (= mbar).

S4. Set-up of chamber experiments

Table S4. Test procedure, steady-state concentration levels and sampling intervals during experiments in the 1 m^3 and 24 m^3 test chamber.

Day no.	**Sampling before doping (background level)**	**Steady-state concentration level [µg m^{-3}] in chamber volume [m^3]**		**Chamber volume [m^3]**		**Sampling intervals [h]**			
		1	**24**	**1**	**24**	**2**	**4**	**5.5**	**7**
1	+	-		-	-	-	-	-	-
2	+	-		-	-	-	-	-	-
3	-	4.4	5.1	+	+	+	+	+	+
4	-	10.0	10.2	+	+	+	+	+	+
5	-	20.1	20.4	+	+	+	+	+	+
6	-	40.0	40.8	+	+	+	+	+	+
7	-	80.1	-	+	-	+	+	+	+
Temperature [°C]				**23±1**	**23±1**				
Relative humidity [%]				**50±3**	**50±3**				
Air exchange rate [h^{-1}]				**1**	**0.5**				

Table S5. Adsorbent media, analytical methods and sampling parameters chosen for comparative measurements during chamber studies.

Adsorber	**Analysis**	**(normative) Reference**	**Air flow rate [mL min^{-1}]**	**Sampling volume [L]**	**Sampling duration [min]**
Carbograph 5TD	TD-GC/MS	Schieweck et al.[6]	125	4	32
DNPH	HPLC/DAD	ISO 16000-3[7]	1000	75	75
	HPLC/MS	-	1000	75	75
DNSH	HPLC/MS	Herrington et al.[8-10]	500	60	120
Tenax TA®	TD-GC/MS	ISO 16000-6[11]	125	4	32

Table S6. Permeation rates of acrolein and toluene given by the manufacturers and calculated on the basis of weight loss measurements as well as the resulting target concentrations in the carrier gas flow. The measured data (mean ± standard deviation) were obtained by active sampling on Carbograph 5TD (C5TD) and Tenax TA®.

	Acrolein		**Toluene**	
	Permeation rate [ng/min]	**Target concentration [µg m^{-3}]**	**Permeation rate [ng min^{-1}]**	**Target concentration [µg m^{-3}]**
Manufacturer information	578 +/- 29	24	992 +/- 248	39
Weight loss measurements	537	22	1178	48
Sampling on C5TD[1]	-	20 ± 1	-	-
Sampling on Tenax TA®[1]	-	7 ± 1	-	40 ± 1

[1] sampling over 14 days testing time: mean values ± standard deviation (SD)

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