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Supplement of

Characterisation and optimisation of a sample preparation method for the detection and quantification of atmospherically relevant carbonyl compounds in aqueous medium

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1 **S1 Experimental**

2 S1.1 Chemicals and standards

3 Cyclohexanone-2,2,6,6-d₄ (98%), methacrolein (95%), acrolein (95%), benzaldehyde ($\geq 99.5\%$), methyl vinyl
4 ketone (99%), glyoxal (40% in water) and 3-methylbutanone (99%) were obtained from Sigma-Aldrich (St. Louis,
5 USA). 2,3- Butanedione (99%) and methyl glyoxal (40% in water) were purchased from Fluka (St. Louis, USA).
6 Dichloromethane (Chromasolv 99,8%) was obtained from Riedel-de Haen (St. Louis, USA) and hexane and
7 toluene as well as *o*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride ($\geq 99\%$) were purchased from
8 Fluka (St. Louis, USA). Isooctane ($\geq 99.5\%$) and chloroform ($\geq 99.8\%$) were obtained from Sigma-Aldrich
9 (St. Louis, USA). Hydrogen peroxide (30% Suprapur[®]) was purchased from Merck KGaA (Darmstadt, Germany).
10 Ultrapure water was used to prepare stock solutions (Milli-Q gradient A 10, 18.2 M Ω /cm², 3 ppb TOC, Millipore,
11 USA).

12

13 **S2 Results**

14 **S2.1 Application of the method**

15 Yu et al. (1995) used the method by Cancilla et al. (1992) to quantify carbonyl compounds formed during the
16 oxidation of isoprene. In addition Lelacheur et al. (1993) developed a PFBHA derivatisation method which was
17 used by Yu et al. (1998) with a subsequent BSTFA (N,O-Bis(trimethylsilyl)trifluoroacetamide) derivatisation step.
18 This method was also used by Jang and Kamens (1999) for the analysis of products originating from the oxidation
19 of α -pinene. Yu et al. (1997) detect carbonyl compounds formed during the oxidation of alkylbenzenes using the
20 improved method of Yu et al. (1995). Carbonyl compounds were also analysed in alcohols using an optimised
21 method by Nawrocki et al. (1996). Additionally, Fick et al. (2003) analysed products formed by the oxidation of
22 α -pinene with the optimised method from Yu et al. (1998). Wardencki et al. (2003) as well as Jelen et al. (2004)
23 analysed carbonyl compounds conducted after the method from Wardencki et al. (2001). Another optimised
24 method which is used by Cancho et al. (2002), Beránek and Kubátová (2008) and van Pinxteren and Herrmann
25 (2013) is the EPA method 556 (Environmental Protection Agency). Furthermore Nambara et al. (1975), Sowinski
26 et al. (2005) and Ortiz et al. (2006) detected carbonyl compounds as well but the methods were not described.

27 **Table S 1:** Analysis of carbonyl compounds involving PFBHA derivatisation methods.

Comment	Detection limits [$\mu\text{mol L}^{-1}$]	Reference	Based on
Analysis of ketosteroids		Nambara et al. (1975)	-
Synthesis of PFBHA			
Analysis of carbonyl compounds in wine		Derevel and Bertrand (1993)	Yamada and Somiya (1989); Glaze et al. (1989)
Analysis of isoprene oxidation products		Yu et al. (1995)	Cancilla et al. (1992)
Analysis of oxidation products from alkylbenzenes		Yu et al. (1997)	Yu et al. (1995)
SPME for extraction of carbonyl compounds	Acrolein 0.2×10^{-2} (LSPME), 0.2×10^{-2} (HSPME); Benzaldehyde 1.0×10^{-2} (LSPME), 0.1×10^{-3} (HSPME); Glyoxal 0.2×10^{-3} (LSPME), 0.9×10^{-2} (HSPME); Methyl glyoxal 0.1×10^{-3} (LSPME), 0.4×10^{-2} (HSPME)	Bao et al. (1998)	Glaze et al. (1989); Lelacheur et al. (1993)
Consecutively derivatisation with BSTFA		Yu et al. (1998)	Lelacheur et al. (1993); Yu et al. (1995)
Analysis of α -pinene oxidation products		Jang and Kamens (1999)	Lelacheur et al. (1993)
SPME for extraction of carbonyl compounds	Glyoxal 0.7×10^{-2} (HSPME); Methylglyoxal 0.4×10^{-2} (HSPME)	Cancho et al. (2002)	EPA method 556
Derivatisation in alcohols	Acrolein 3.0×10^{-2} (LLE), 0.2×10^{-2} (SPME)	Wardencki et al. (2001)	Nawrocki et al. (1996)
Analysis of α -pinene oxidation products in dependence of OH radical concentration, relative humidity and time		Fick et al. (2003)	Yu et al. (1998)
SPME for extraction of carbonyl compounds		Wardencki et al. (2003)	Wardencki et al. (2001)
SPME for extraction of C_3 - C_{10} aliphatic aldehydes		Jelen et al. (2004)	Wardencki et al. (2001)
Headspace analysis		Sowinski et al. (2005)	-
Analysis in spirits and vodka			
Denuder-filter sampling		Ortiz et al. (2006)	-
Analysis of bifunctional carbonyl compounds			
Consecutively derivatisation with BSTFA			
Solid phase microextraction of aldehydes		Beránek and Kubátová (2008)	EPA method 556
Glyoxal and Methylglyoxal in atlantic seawater	Glyoxal 0.1×10^{-2} (sea water); Methyl glyoxal 0.1×10^{-3} (sea water)	Van Pinxteren and Herrmann (2013)	EPA method 556

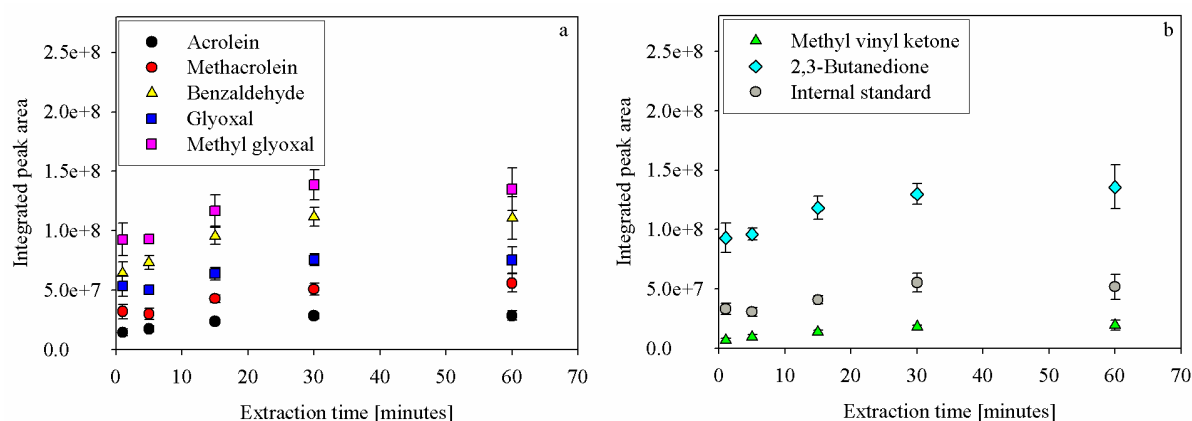
28 SPME: solid phase micro extraction; BSTFA: N,O-Bis(trimethylsilyl)trifluoroacetamide; TMCS:
 29 trimethylchlorosilane; LLE: liquid-liquid extraction; LSPME: liquid solid phase micro extraction; HSPME:
 30 headspace solid phase micro extraction
 31

32 S2.2 Detection limits

33 Further detection limits are determined in the literature. Detection limits given by Serrano et al. (2013) cannot be
34 compared with the data obtained in the present study as a completely different extraction technique, namely micro
35 liquid-liquid extraction (MLLE) was used in this study. MLLE leads to much higher preconcentration depending
36 on the sample volume that cannot be compared to the extraction technique used in the present study. Furthermore
37 Serrano et al. (2013) used a large volume injection of 20 – 50 μL leading to higher detection limits as well.
38 Therefore better detection limits by a factor of 100 for benzaldehyde, 1000 for glyoxal and 10000 for methyl
39 glyoxal were determined (Serrano et al., 2013). The detection limits determined by EPA method 556,
40 Bao et al. (1998), Cancho et al. (2002) and Wardencki et al. (2001) are not comparable to the detection limits
41 found in the present study as well because an electron capture detection (ECD) was used which has a better
42 sensitivity than the detection with mass spectrometer. The better sensitivity of the ECD was also observed by
43 Glaze et al. (1989) comparing the detection limits of the oximes measured with mass spectrometer and electron
44 capture detection. Therefore they achieved detection limits between 0.1×10^{-3} and $0.01 \mu\text{mol L}^{-1}$ for the different
45 carbonyl compounds. In comparison the lowest detection limit determined with mass spectrometer in this study
46 was $0.01 \mu\text{mol L}^{-1}$ for glyoxal and benzaldehyde. Furthermore van Pinxteren and Herrmann (2013) analysed sea
47 water samples after a preconcentration of 100 to 200. Therefore the samples are more concentrated than in the
48 presented study leading to lower detection limits. Seaman et al. (2006) determined detection limits with an ECD
49 for acrolein, methacrolein, methyl vinyl ketone, glyoxal, methyl glyoxal and benzaldehyde in the gas phase and
50 not in the aqueous phase. Thus the detection limits have been determined for gas phase measurements and are not
51 comparable to the present method.

53 S2.3 Extraction time

54 *Extraction with dichloromethane*



55 **Figure S 1:** Dependency of the peak area of aldehydes (a: acrolein, black; methacrolein, red; benzaldehyde, yellow; glyoxal, blue), methyl glyoxal (a, pink), ketones (b: methyl vinyl ketone, green; 2,3-butanedione, turquoise) and the internal standard (b, grey) on the extraction time with dichloromethane.

56 **Table S 2:** Extraction efficiency of the investigated carbonyl compounds.

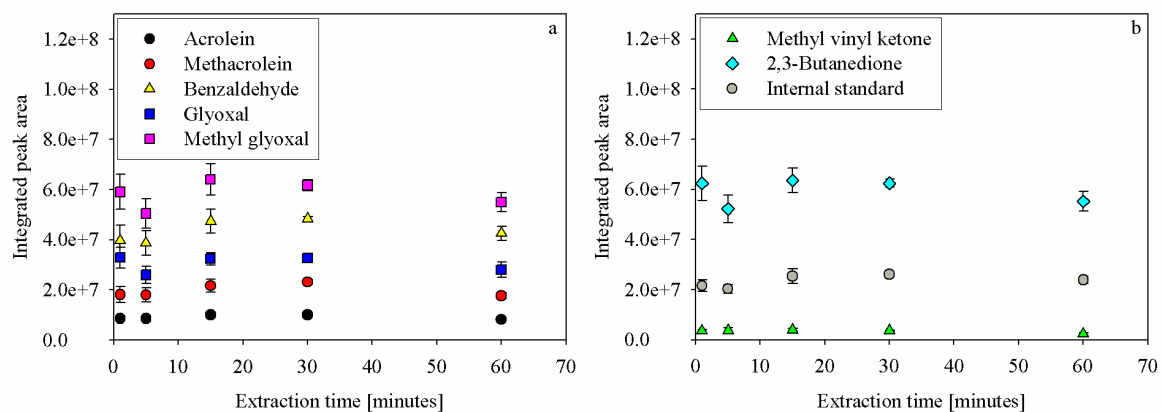
Carbonyl compound	Extraction efficiency [%]		
	1. Extraction	2. Extraction	3. Extraction
Acrolein	97 ± 2	3 ± 2	0
Methacrolein	98 ± 1	2 ± 1	0
Methyl vinyl ketone	98 ± 2	2 ± 2	0
Benzaldehyde	98 ± 2	2 ± 2	0
Glyoxal	99 ± 1	1 ± 1	0
Methyl glyoxal	98 ± 2	2 ± 2	0
2,3-Butanedione	97 ± 2	3 ± 2	0
Internal standard	96 ± 2	4 ± 2	0

57

58

59 *Extraction with hexane*

60 The effect of the extraction time was also evaluated using hexane as an extraction solvent and the results are
61 shown in Figure S 2.



62 **Figure S 2:** Dependency of the peak area of aldehydes (a: acrolein, black; methacrolein, red; benzaldehyde, yellow; glyoxal, blue), methyl glyoxal
63 (a, pink), ketones (b: methyl vinyl ketone, green; 2,3-butanedione, turquoise) and the internal standard (b, grey) from the extraction time extracted
64 with hexane.

62

63

64 It can be seen that hexane shows the same results as it was found for dichloromethane. After 30 minutes the
65 extraction was almost completed. Thus, it is expected that shorter extraction times cause a significant
66 underestimation of the carbonyl compound peak areas with hexane as well. However, as hexane is the most
67 commonly used extraction solvent an effort was made to determine correction factors for the different extraction
68 solvents to enable assignability between the existing methods and the optimised method presented in this study.
69 Therefore, two sets of samples were prepared. The first set was extracted using an extraction with dichloromethane
70 for 30 minutes whereas the second set was extracted with hexane. As different extraction times can be found in
71 the literature correction factors were determined for 1 to 60 minutes of hexane extraction (Table S 3) determined
72 through the ratios of the peak areas extracted with hexane and dichloromethane.

73 **Table S 3:** Correction factors for the extraction of carbonyl compounds with hexane for an extraction time
 74 between 1 and 60 minutes in relation to an extraction time of 30 minutes with dichloromethane.

Carbonyl compound	Extraction time hexane [minutes]				
	1	5	15	30	60
Acrolein	3.33 ± 0.45	3.37 ± 0.27	2.85 ± 0.35	2.82 ± 0.22	3.45 ± 0.19
Methacrolein	2.87 ± 0.61	2.86 ± 0.30	2.38 ± 0.39	2.21 ± 0.28	2.88 ± 0.10
Methyl vinyl ketone	5.36 ± 0.87	5.34 ± 1.66	4.74 ± 0.74	5.06 ± 0.58	7.86 ± 1.05
Benzaldehyde	2.88 ± 0.63	2.91 ± 0.18	2.37 ± 0.30	2.31 ± 0.15	2.63 ± 0.09
Glyoxal	2.32 ± 0.30	2.94 ± 0.32	2.34 ± 0.21	2.31 ± 0.18	2.72 ± 0.31
Methyl glyoxal	2.37 ± 0.35	2.76 ± 0.18	2.17 ± 0.23	2.25 ± 0.24	2.52 ± 0.19
2,3-Butanedione	2.10 ± 0.30	2.50 ± 0.15	2.06 ± 0.23	2.09 ± 0.19	2.36 ± 0.12
Internal standard	2.59 ± 0.58	2.71 ± 0.17	2.22 ± 0.50	2.12 ± 0.34	2.31 ± 0.20

75 The strongest dependency towards the extraction solvent was found for methyl vinyl ketone (7.86 ± 1.05) and
 76 weakest for 2,3-butanedione (2.06 ± 0.23). With the obtained correction factors an underestimation of the
 77 carbonyl compound concentration caused by a less effective extraction with hexane can be corrected.

78

79 **S2.4 Derivatisation time**

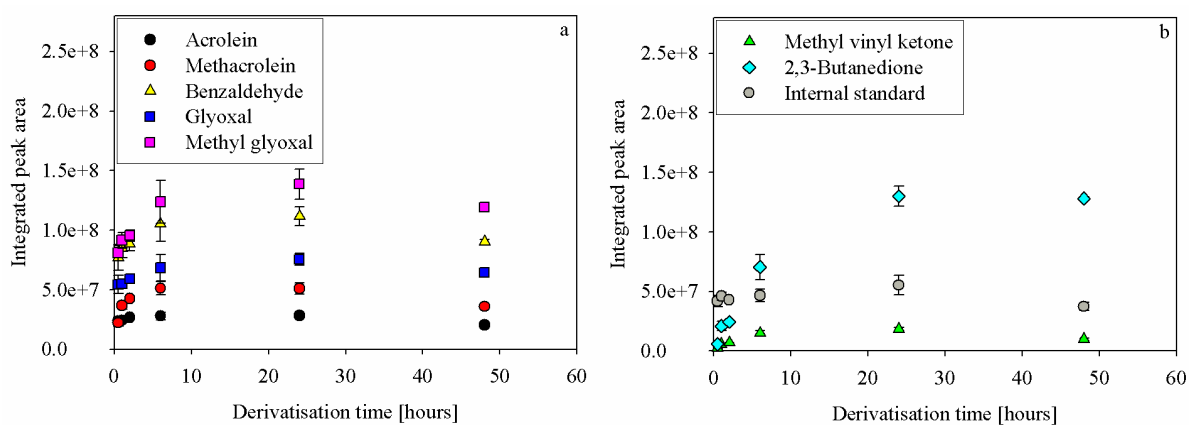


Figure S 3: Influence of the derivatisation time on the integrated peak area of aldehydes (a: acrolein, black; methacrolein, red; benzaldehyde, yellow; glyoxal, blue), methyl glyoxal (a, pink), ketones (b: methyl vinyl ketone, green; 2,3-butanedione, turquoise) and the internal standard (b, grey).

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81 **S2.5 Amount of PFBHA in the derivatisation**

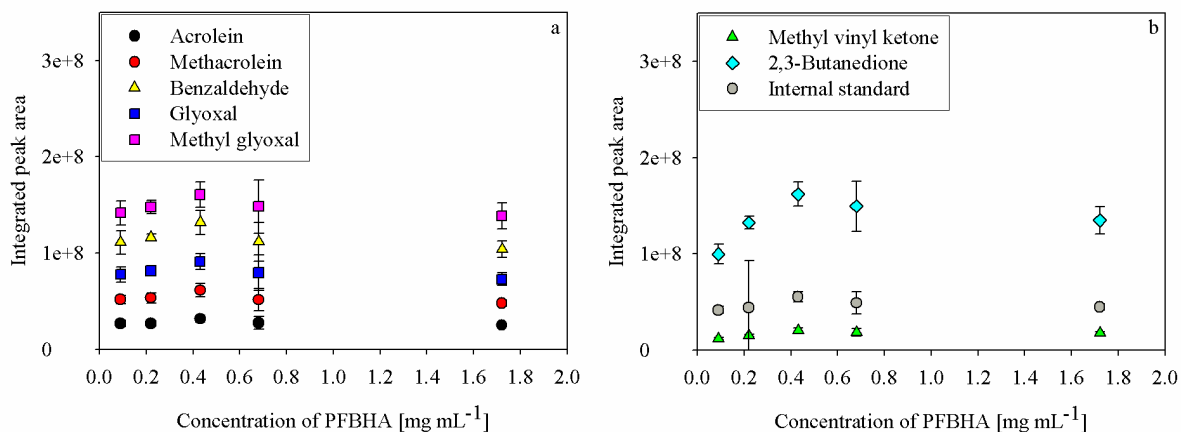


Figure S 4: Dependency of the integrated peak area of investigated aldehydes (a: acrolein, black; methacrolein, red; benzaldehyde, yellow; glyoxal, blue), methyl glyoxal (a, pink) and ketones (b: methyl vinyl ketone, green; 2,3-butanedione, turquoise) as a function of PFBHA concentration in the sample solution. Please note, the internal standard is given in grey (b).

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83

84 **S2.6 pH value during derivatisation and extraction**

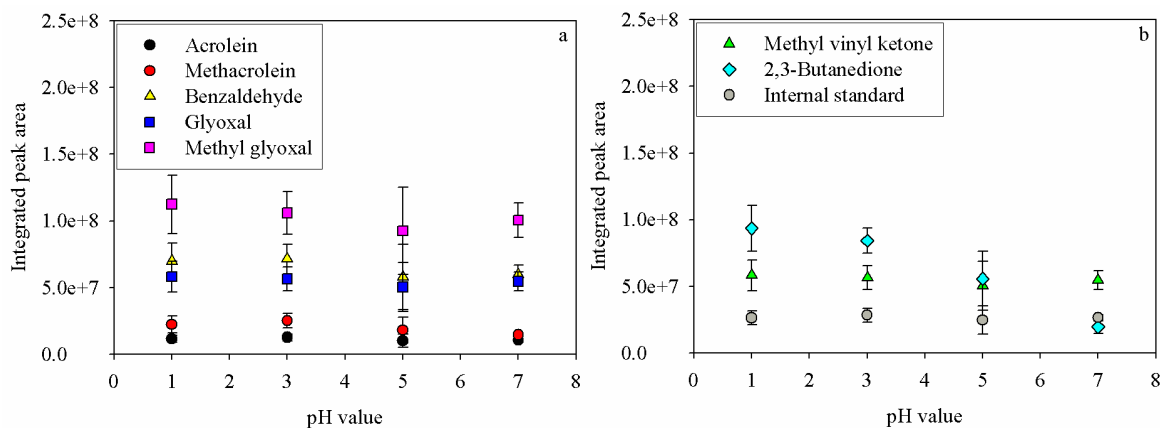


Figure S 5: Influence of the pH value on the derivatisation reaction of aldehydes (a: acrolein, black; methacrolein, red; benzaldehyde, yellow; glyoxal, blue), methyl glyoxal (a, pink), ketones (b: methyl vinyl ketone, green; 2,3-butanedione, turquoise) and the internal standard (b, grey).

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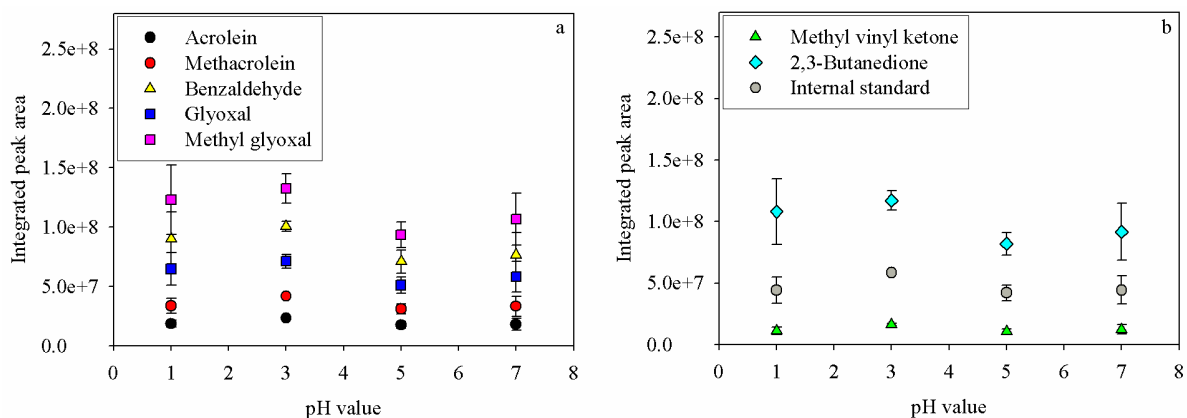


Figure S 6: Influence of the pH value on the extraction efficiency of aldehydes (a: acrolein, black; methacrolein, red; benzaldehyde, yellow; glyoxal, blue), methyl glyoxal (a, pink), ketones (b: methyl vinyl ketone, green; 2,3-butanedione, turquoise) and the internal standard (b, grey).

86

87 S2.7 Proof of principle

88 The optimised method (dichloromethane as extraction solvent, 30 minutes extraction time, 24 h derivatisation
89 time, 0.43 mg mL⁻¹ PFBHA, pH = 3 for the derivatisation and pH = 1 for the extraction) was applied to a series
90 of stock solutions. The concentrations of the seven target carbonyl compounds were varied in a range of 2 to
91 16 μmol L⁻¹ (Figure S 7, supplementary material S 2.7). From the repetitive analysis of the dilution series a R² of
92 0.99 and detection limits between 0.01 and 0.17 μmol L⁻¹ were achieved (Table 3).

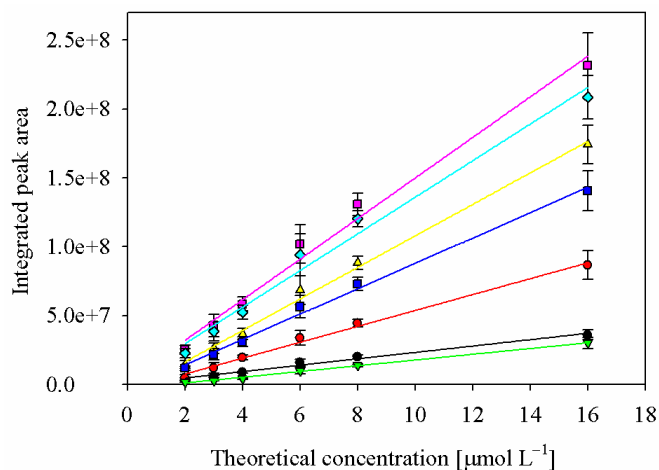


Figure S 7: Calibration curve for acrolein (black, R² = 0.987), methacrolein (red, R² = 0.993), methyl vinyl ketone (green, R² = 0.997), benzaldehyde (yellow, R² = 0.996), glyoxal (blue, R² = 0.995), methyl glyoxal (pink, R² = 0.984) and 2,3-butanedione (turquoise, R² = 0.984) in the concentration range of 2 to 16 μmol L⁻¹.

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