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

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## S 1 Experimental

### S 1.1 Chemicals and standards

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

### S 1.2 Batch reactor experiment

Experiments were conducted in a 300 mL batch reactor containing a 0.1 mmol L$^{-1}$ solution of 3-methylbutanone and a 10 mmol L$^{-1}$ hydrogen peroxide solution. The photolysis of hydrogen peroxide with a xenon-mercury lamp (500 W; L.O.T.- Oriel GmbH & Co. KG, Darmstadt, Germany) was used as OH radical source. The reaction mixture was continuously stirred over the course of the experiment and 3 mL samples were taken after each hour. The samples were treated as described in section 2.1 ("*Sample preparation*").

### S 1.3 Instrumentation

The samples were analysed using a 6890 Series GC System (Agilent Technologies, Santa Clara, USA) coupled with an electron ionisation quadrupole mass spectrometer (Agilent 5973 Network mass selective detector, Santa Clara, USA). For separation a HP-5MS UI column (Agilent J & W GC columns, 30 m × 0.25 mm × 0.25 µm) was used. The temperature program was as follows: 50 °C isothermal for 2 minutes and elevated to 230 °C with 10 °C minute$^{-1}$. The temperature of 230 °C was held for 1 minute. The temperature gradient ended with 320 °C which was held constant for 10 minutes. The inlet was operated in the splitless mode at a temperature of 250 °C.

## S 2 Results

### S 2.1 Application of the method

A headspace analysis was applied by Schmarr et al. (2008) but the derivatisation was adopted from Cancilla et al. (1992). Also Yu et al. (1995) used the method by Cancilla et al. (1992) to quantify carbonyl compounds formed during the oxidation of isoprene. In addition Lelacheur et al. (1993) developed a PFBHA derivatisation method which was used by Yu et al. (1998) with a subsequent BSTFA (N,O-Bis(trimethylsilyl)trifluoroacetamide) derivatisation step. This method was also used by Jang and Kamens (1999) for the analysis of products originating from the oxidation of α-pinene. Yu et al. (1997) detect carbonyl compounds formed during the oxidation of alkylbenzenes using the improved method of Yu et al. (1995). Carbonyl compounds were also analysed in alcohols using an optimised method by Nawrocki et al. (1996). Additionally, Fick et al. (2003) analysed products formed by the oxidation of α-pinene with the optimised method from

Yu et al. (1998). Wardencki et al. (2003) as well as Jelen et al. (2004) analysed carbonyl compounds conducted after the method from Wardencki et al. (2001). Another optimised method which is used by Cancho et al. (2002), Beránek and Kubátová (2008) and van Pinxteren and Herrmann (2013) is the EPA method 556 (Environmental Protection Agency). Furthermore Nambara et al. (1975), Sowinski et al. (2005) and Ortiz et al. (2006) detected carbonyl compounds as well but the methods were not described.

**Table S 1:** Applications of the PFBHA method.

| **Comment** | **Detection limits [µmol $L^{-1}$]** | **Reference** | **Based on** |
|---|---|---|---|
| Analysis of ketosteroids<br>Synthesis of PFBHA | | Nambara et al. (1975) | - |
| 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 $0.2 \times 10^{-2}$ (LSPME), $0.2 \times 10^{-2}$ (HSPME); Benzaldehyde $1.0 \times 10^{-2}$ (LSPME), $0.1 \times 10^{-3}$ (HSPME); Glyoxal $0.2 \times 10^{-3}$ (LSPME), $0.9 \times 10^{-2}$ (HSPME); Methyl glyoxal $0.1 \times 10^{-3}$ (LSPME), $0.4 \times 10^{-2}$ (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 $0.7 \times 10^{-2}$ (HSPME); Methylglyoxal $0.4 \times 10^{-2}$ (HSPME) | Cancho et al. (2002) | EPA method 556 |
| Derivatisation in alcohols | Acrolein $3.0 \times 10^{-2}$ (LLE), $0.2 \times 10^{-2}$ (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<br>Analysis in spirits and vodka | | Sowinski et al. (2005) | - |
| Denuder-filter sampling<br>Analysis of bifunctional carbonyl compounds<br>Consecutively derivatisation with BSTFA | | Ortiz et al. (2006) | - |
| Headspace analysis | | Schmarr et al. (2008) | Cancilla et al. (1992) |
| Solid phase microextraction of aldehydes | | Beránek and Kubátová (2008) | EPA method 556 |
| Glyoxal and Methylglyoxal in atlantic seawater | Glyoxal $0.1 \times 10^{-2}$ (sea water); Methyl glyoxal $0.1 \times 10^{-3}$ (sea water) | Van Pinxteren and Herrmann (2013) | EPA method 556 |

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

## S 2.2 Detection limits

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

## S 2.3 Extraction time

*Extraction with dichloromethane*

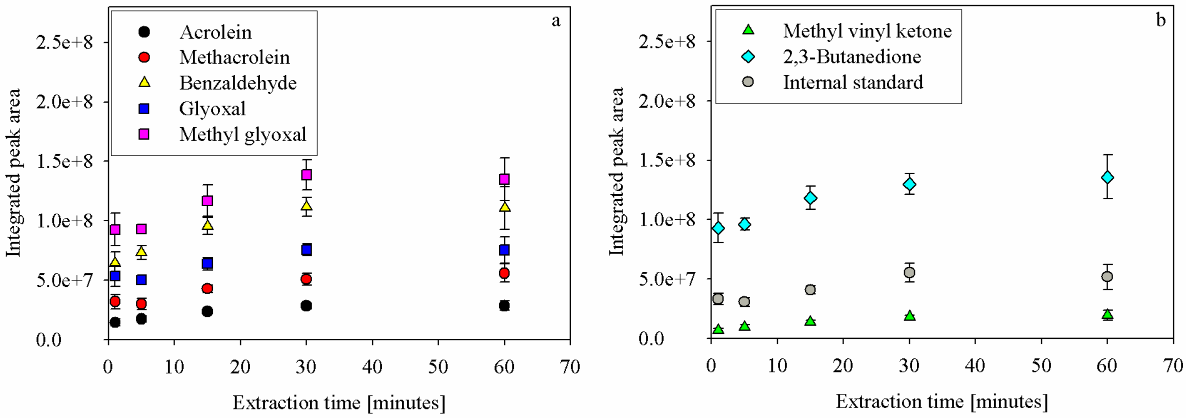

**Figure S 1:** Dependency of the peak area of aldehydes (a: acrolein, black; methacrolein, red; benzaldehyde, yellow; glyoxal, blue), methyl glyoxal (a, pink), ketones (b: methyl vinyl ketone, green; 2,3-butanedione, turquoise) and the internal standard (b, grey) on the extraction time with dichloromethane.

**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 |

*Extraction with hexane*

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

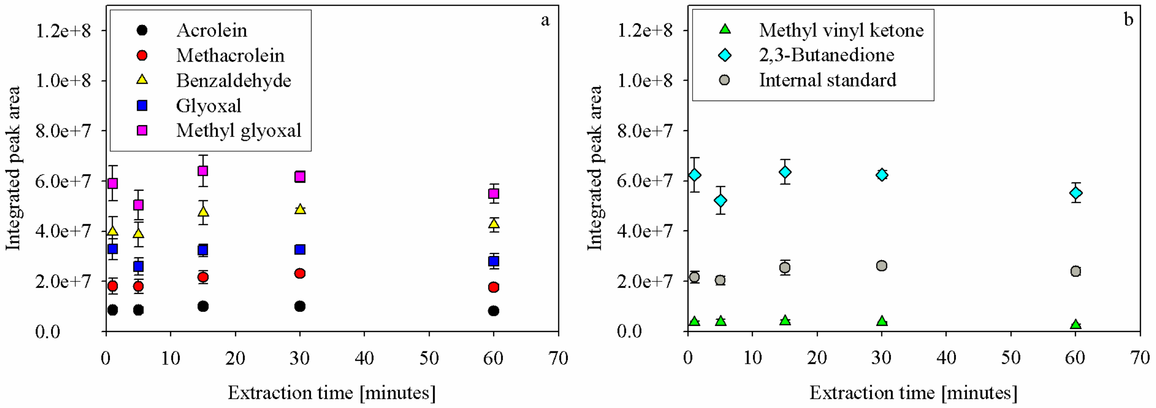

**Figure S 2:** Dependency of the peak area of aldehydes (a: acolein, black; methacrolein, red; benzaldehyde, yellow; glyoxal, blue), methyl glyoxal (a, pink), ketones (b: methyl vinyl ketone, green; 2,3-butanedione, turquoise) and the internal standard (b, grey) from the extraction time extracted with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

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

**Table S 3:** Correction factors for the extraction of carbonyl compounds with hexane 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 |

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

## S 2.4 Derivatisation time

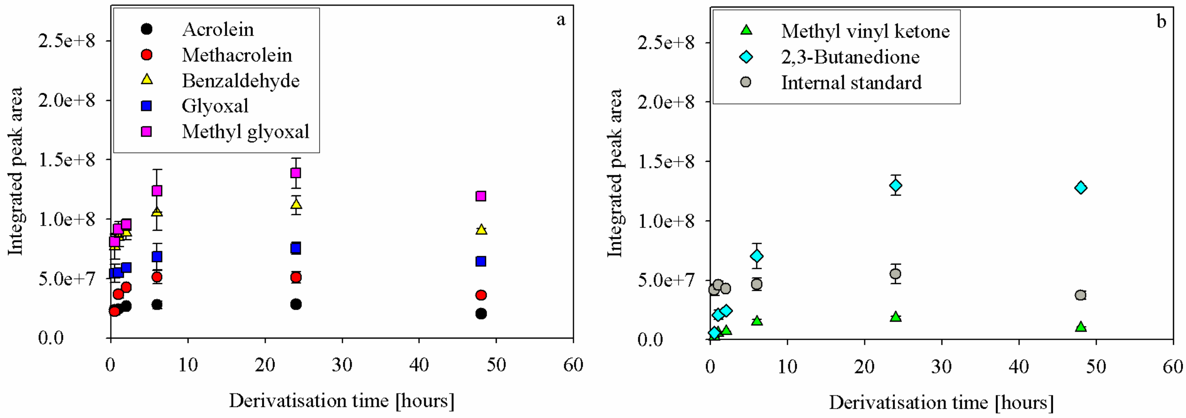

**Figure S 3:** Influence of the derivatisation time on the integrated peak area of aldehydes (a: acrolein, black; methacrolein, red; benzaldehyde, yellow; glyoxal, blue), methyl glyoxal (a, pink), ketones (b: methyl vinyl ketone, green; 2,3-butanedione, turquoise) and the internal standard (b, grey).

## S 2.5 Amount of PFBHA in the derivatisation

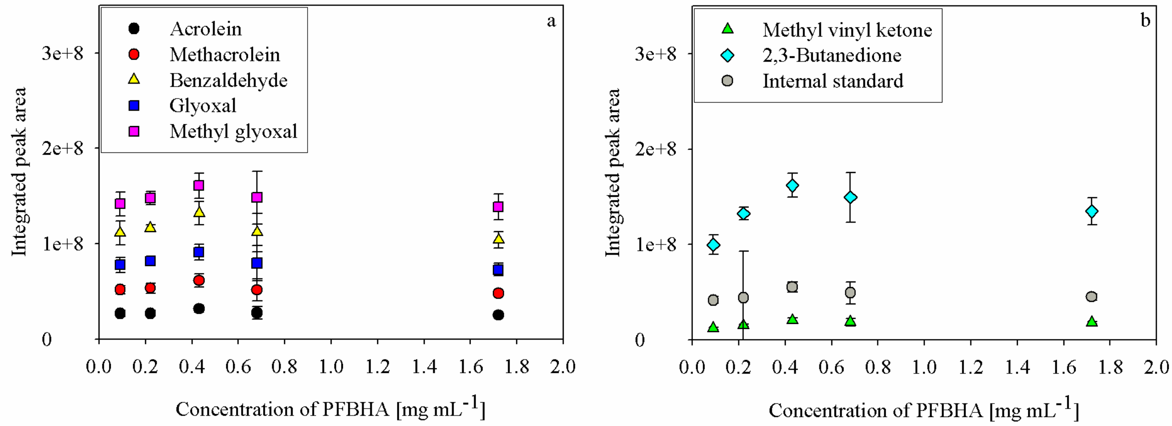

**Figure S 4:** Dependency of the integrated peak area of aldehydes (a: acrolein, black; methacrolein red; benzaldehyde, yellow; glyoxal blue), methyl glyoxal (a, pink), ketones (b: methyl vinyl ketone, green; 2,3-butanedione, turquoise and the internal standard (b, grey) on the added amount of PFBHA.

## S 2.6 pH value during derivatisation and extraction

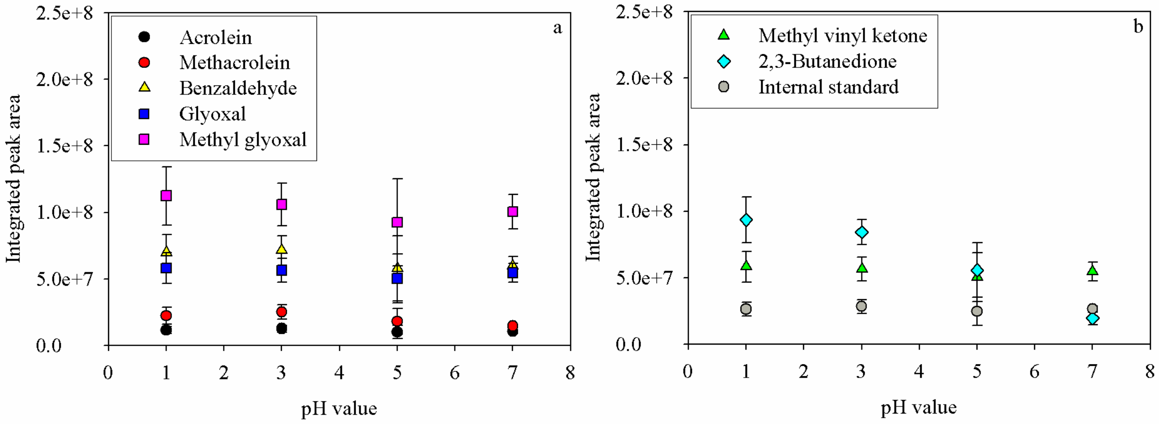

**Figure S 5:** Influence of the pH value on the derivatisation reaction of aldehydes (a: acrolein, black; methacrolein, red; benzaldehyde, yellow; glyoxal, blue), methyl glyoxal (a, pink), ketones (b: methyl vinyl ketone, green; 2,3-butanedione, turquoise) and the internal standard (b, grey).

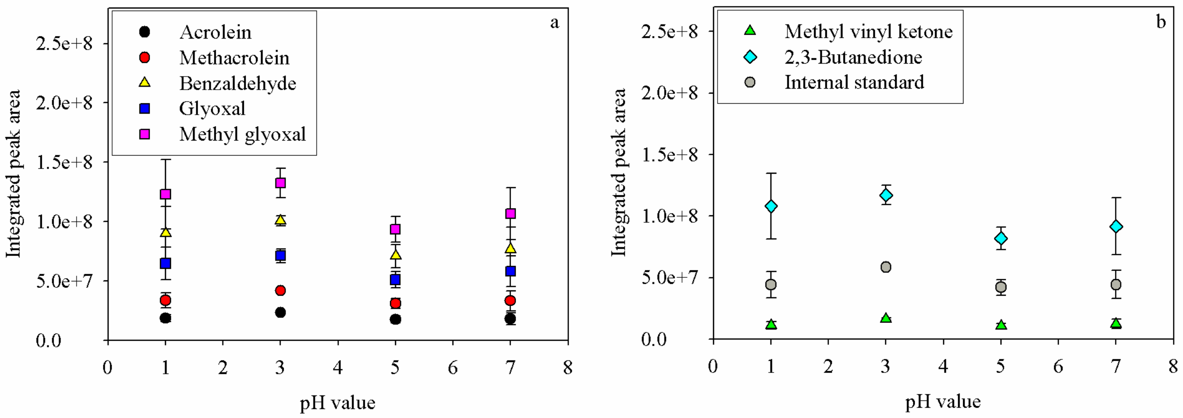

**Figure S 6:** Influence of the pH value on the extraction efficiency of aldehydes (a: acrolein, black; methacrolein, red; benzaldehyde, yellow; glyoxal, blue), methyl glyoxal (a, pink), ketones (b: methyl vinyl ketone, green; 2,3-butanedione, turquoise) and the internal standard (b, grey).

## S 2.7 Evaluation of the optimised method and application

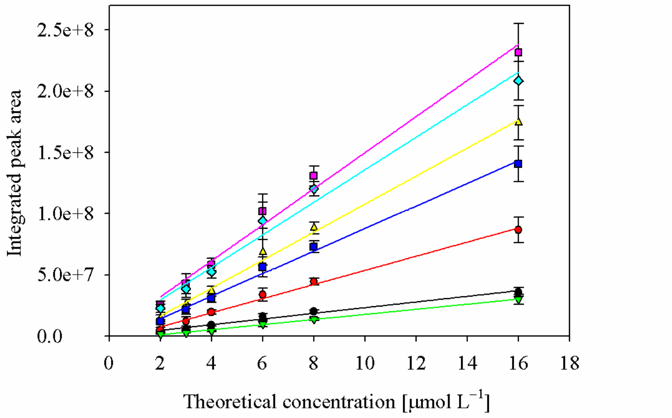

**Figure S 7:** Calibration curve for the carbonyl compounds acrolein (black, R² = 0.987), methacrolein (red, R² = 0.993), methyl vinyl ketone (green, R² = 0.997), benzaldehyde (yellow, R² = 0.996), glyoxal (blue, R² = 0.995), methyl glyoxal (pink, R² = 0.984) and 2,3-butanedione (turquoise, R² = 0.984) obtained from the optimised method.

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