Responses to the Reviewers' Comments:

We thank the reviewers for the consideration and the constructive comments. The manuscript is revised based on the suggestions made and detailed responses to the reviewers are given in the following:

Referee #3

This paper reports the methodological optimization of sample preparation for analysis by GC/MS of seven carbonyl compounds. The paper compares these optimizations with prior literature optimizations and an EPA method. The paper presents some novel findings and some findings that agree with literature. However, I do have a few questions/concerns regarding this paper.

Major Corrections

1) Sections 3.1 – 3.4: There are multiple positive and negative effects determined by this study. It is difficult to follow some of the comparisons with literature optima when multiple parameters vary at once. For example on Page 864, Lines 4, 6 and 20: there are effects due to compound saturation and "size" as well as derivatization temperature.

Authors' comment

To improve and clarify the three section were rewritten as follows:

Page 862 Line 6-13: *'Hexane, dichloromethane, toluene and chlorobenzene were reported in the literature as suitable extraction solvents (Spaulding and Charles, 2002; Ye et al., 2011; Glaze et al., 1989; Strassnig et al., 2000). Within the present study these reported extraction solvents (hexane, dichloromethane, toluene) were investigated as well, in addition to isooctane and chloroform. Figure 1 illustrates the influence of the extraction solvent on the amount of detected carbonyl compounds. Surprisingly, from the comparison dichloromethane turned out as the most effective extraction solvent, that was among numerous of studies only described by Spaulding and Charles (2002). This is in contrast to former studies where hexane was commonly used as extraction solvent (EPA method 556; Glaze et al., 1989; Lelacheur et al., 1993; Seaman et al., 2006; Serrano et al., 2013).'*

Page 862 Line 16-18: *'Notably, toluene is recommended in the literature as extraction solvent (Strassnig et al., 2000). This can be confirmed at least for the extraction of benzaldehyde. The better extraction of benzaldehyde with toluene is likely due to the aromatic character of both toluene and benzaldehyde.*

Detection limits were determined for the present study in the single ion mode (SIM) based on a signal to noise ratio (S/N) of ≥ 3 and compared to those reported by Glaze et al. (1989).'

Page 862 Line 20 – 863 Line 2: *'In the case of acrolein this preconcentration results in a detection limit of 0.17 µmol L^{-1} that is improved by a factor of ≈ 2 compared to Glaze et al. (1989). The detection limit of other investigated compounds showed an improvement by about a factor of 10. The detection limits were as follows: 0.01± 0.0003µmol L^{-1} for benzaldehyde, 0.01 ± 0.0004 µmol L^{-1} for methyl glyoxal and 0.01 ± 0.0006 µmol L^{-1} for glyoxal (for more details see S2.2 and Table 3). Based on the low standard deviations, it can be stated that the extraction with dichloromethane results in a high reproducibility.*
Due to the high reproducibility and low detection limits, dichloromethane was chosen as extraction solvent.'

Page 863 Line 4 -6: *'In addition to the extraction solvent, it was found that the extraction time had a significant influence on the quantity of the extracted amount of derivatised carbonyl compound (Fig. S1; Supplement S2.3).'*

Page 863 Line 8 – 23: *'This is different from previous findings with 2 min (Ye et al., 2011) and 3 min extraction time (EPA method 556). However, the data set on the influence of the extraction time is scarce and no further method development was found in the literature examining this issue. Furthermore most of studies in the past used very short extraction times (e.g. Glaze et al., 1989; Lelacheur et al., 1993; Serrano et al., 2013). These shorter extraction times likely cause significant lower peak areas of the oximes and therefore higher detection limits (Table 3). Furthermore, the incomplete extraction caused by the short extraction times might lead to a decreasing reproducibility.*
To ensure a complete extraction of the analytes, the extraction time was extended to 30 min, and the extraction procedure was repeated three times. After the first extraction the amount of detected oxime was negligibly small (≈ 2 %, Table S 2; Supplement S2.3) indicating an almost complete extraction within 30 min e.g., methyl vinyl ketone, benzaldehyde and methyl glyoxal showed an extraction efficiency of 98 % ± 2 % after the first extraction. Based on this, an extraction time of 30 min can be recommended. Because hexane is the commonly used extraction solvent, the influence of the extraction time was also investigated for hexane. The extraction with hexane showed the same results regarding the extraction time as it was found for dichloromethane. Thus the extraction was complete after an extraction time of 30 min. To ensure, the comparability of hexane (commonly used) and dichloromethane extraction factors were determined (see Supplement S2.3).'

Page 863 Line 25 – 864 Line 9: *'The influence of the derivatisation time was evaluated using a duration ranging from 0.5 to 48 h (Fig. S3, Supplement S2.4). For all the investigated carbonyl compounds it was found that the reaction was almost completed after 24 h. Thus, it can be recommended to use a derivatisation time of 24 h, that is in good agreement to the findings by Lelacheur et al. (1993) and Kobayashi et al. (1980). Nevertheless, optimised derivatisation times can be found ranging from 20 s to 96 h for the carbonyl compounds investigated in the literature studies (EPA method 556; Glaze et al., 1989; Hudson et al., 2007; Kobayashi et al., 1980; Lelacheur et al., 1993; Saison et al., 2009; Seaman et al., 2006; Serrano et al., 2013; Strassnig et al., 2000; Sugaya et al., 2004; Takeuchi et al., 2007). Among various compounds investigated in the literature the atmospheric relevant compounds formaldehyde, acetaldehyde, butanal, methyl ethyl ketone and methyl butyl ketone were used (Glaze et al., 1989).'*

Page 864 Line 11 – 13: *'The difference between that study and the results obtained within the present study might be caused by the carbonyl compounds used for the optimisation.'*

Page 864 Line 17 – 20: *'Nevertheless, a shorter derivatisation time of 2-4 h has also been reported in literature where, however, only acetone and formaldehyde (Hudson et al., 2007; Takeuchi et al., 2007) were considered.'*

Page 864 Line 26 – 865 Line 1: *'After the carbonyl-bisulfite adduct was formed, hydrogen peroxide was added to destroy the formed adduct and to yield carbonyl compounds which were directly derivatised with PFBHA.'*

Page 865 Line 2: *'Certain few studies optimising derivatisation with PFBHA cannot be considered for a comparison because they were conducted under higher temperatures (EPA method 556; Serrano et al., 2013; Sugaya et al., 2004) or they used microwave-assisted derivatisation (Strassnig et al., 2000).'*

Page 864 Line 4: Are the times listed on Line 4 for just the seven target compounds of this study?

Authors' comment

The derivatisation times listed in Line 4 refer to all compounds investigated in the cited literature studies. Thus there are other carbonyl compounds as the seven compounds used for this study. To clarify this issue, the sentence is changed to *'Nevertheless, optimised derivatisation times can be found ranging from 20 s and 96 h for the carbonyl compounds investigated in literature studies (EPA method 556; Glaze et al., 1989; Hudson et al., 2007;*

Kobayashi et al., 1980; Lelacheur et al., 1993; Saison et al., 2009; Seaman et al., 2006; Serrano et al., 2013; Strassnig et al., 2000; Sugaya et al., 2004; Takeuchi et al., 2007).'

Are the magnitudes of each of the positive and negative effects on LOD the same for each parameter optimized in this study?

Authors' comment

No, the effects are different - as it can be seen in Fig. 1, Fig. S1 and Fig. S3 - S6 the derivatisation reagent as well as the derivatisation and extraction time have the strongest effect on the integrated peak areas of the carbonyl compounds. The pH values or the PFBHA amount showed only a minor influence. However, the optimal extraction solvent dichloromethane showed the highest effect on the integrated peak areas of the carbonyl compounds in comparison to the commonly used hexane. Thus the extraction solvent has probably the strongest influence on the detection limits and is one of the most important improvement of the present method optimisation.

Can the comparisons be clarified?

Authors' comment

Based on the first comment of the reviewer the section was rewritten.

2) Page 865, Lines 8 – 11: There is an apparent competitive effect at high PFBHA concentrations. Is the optimal amount of PFBHA influenced by which organic solvent is used? In other words is the optimum amount of PFBHA the same in hexane and dichloromethane?

Authors' comment

The effect of the PFBHA amount using hexane as extraction solvent was not examined in the present study because dichloromethane enhanced the extraction of the carbonyl compounds significantly. Note that the extraction solvent relating to the PFBHA amount can only have an influence on the detection of the carbonyl compounds due to the transfer of PFBHA in the organic phase. This transfer leads to a less effective extraction of the oximes caused by the increasing amount of PFBHA in the organic phase. This is also reported by Saison et al. (2009). In the literature study by Seaman et al. (2006) the PFBHA amount was optimised using hexane for the extraction. These authors found an optimal result with a PFBHA concentration of 0.2 mg mL^{-1} witch is smaller than the optimal PFBHA concentration found in the present study. Thus, it is possible that the use of hexane leads to another optimal amount of PFBHA.

3) The sample preparation section (2) is missing the details of the preparation of the 3-methylbutanone solution and the method of generation of OH radicals in aqueous solution.

Authors' comment

The description of the bulk reactor experiment is removed from the supplement (Page 1 Line 12 – 17; S 1.2) and included in the experimental section of the main text (Page 861 Line 7). Furthermore the sentence (Page 861 Line 5 – 6) is changed to *'For further information about the chemicals and standards see Supplement S1.'*

4) Page 872: If in the table, Spaulding and Charles (2002) found dichloromethane to be the optimal solvent, why does Page 862, Line 8 state that the dichloromethane effectivity is "surprising"?

Authors' comment

Most of the literature studies (e.g. Glaze et al., 1989; EPA method 556) used hexane as extraction solvent. Thus it was surprising that dichloromethane shows such a significant improvement of the extraction which was found by one further literature study (Spaulding and Charles, 2002). For clarification the sentence was changed as following: *'Surprisingly, from the comparison dichloromethane turned out as the most effective extraction solvent, that was among numerous of studies only described by Spaulding and Charles (2002).'*

Page 862 Line 12: this implies hexane was optimal while dichloromethane and chlorobenzene were "good" but not optimal. Which is correct: Page 872 or Page 862, Lines 8 and 12?

Authors' comment

Dichloromethane was found as an optimal extraction solvent. In Fig. 1 higher integrated peak areas of the carbonyl compounds were found after the extraction with dichloromethane than with hexane. The sentence should only mention, that in addition to hexane dichloromethane and chlorobenzene were used as extraction solvent in the literature as well. The sentence (Page 862 Line 11 - 13) is deleted during the rewriting of the section.

5) The term "reagent" (as in Page 862, Line 2 and after) may be misleading when referring to an extraction solvent since the organic solvents do not take part in the derivatization reaction(s) and are added after derivatization is considered complete.

Authors' comment

The term '*extracting reagent*' is changed to '*extraction solvent*' in the whole manuscript and in the supplement.

6) Page 875: This figure appears to have positive error bars but not negative error bars. Some error bars are rather large and may actually overlap the mean peak areas of other solvents. Are the error bars standard deviations? The main text compares solvent peak areas but doesn't mention the uncertainty seen in Figure 1. Given the error bars, can the solvents be considered different in effectivity?

Authors' comment

Fig. 1 is changed to have positive and negative error bars. The error bars are the standard deviations (three repetitions).

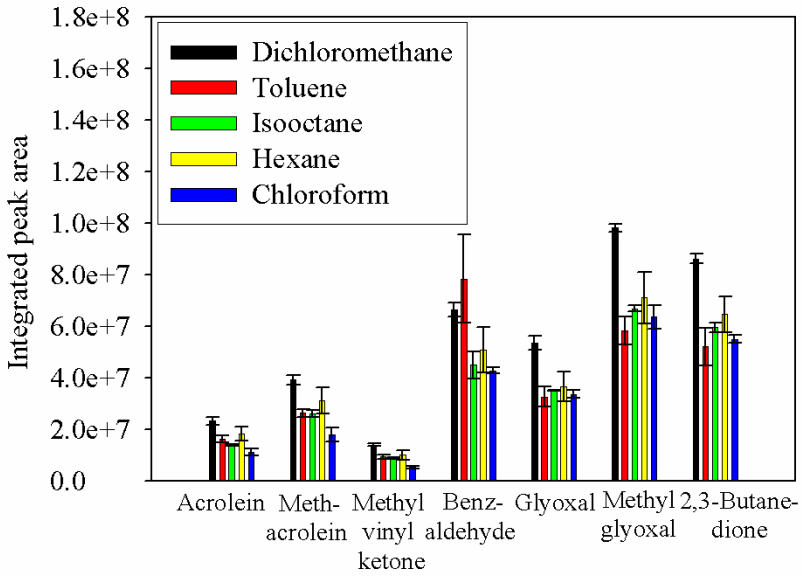

Figure 1. Influence of the extraction solvent dichloromethane (black), toluene (red), isooctane (green), hexane (yellow) and chloroform (blue) on the integrated peak areas of the standard compounds acrolein, methacrolein, methyl vinyl ketone, benzaldehyde, glyoxal, methyl glyoxal and 2,3-butanedione.

For most of the target compounds the error bars are the smallest for the extraction with dichloromethane (between 2% and 7% regarding to the peak areas). Only for benzaldehyde the smallest error bars were found with chloroform (≈ 3%). In comparison the highest error bars for acrolein, methacrolein, methyl vinyl ketone, glyoxal and methylglyoxal were found with hexane (between 11% and 22%). For benzaldehyde and 2,3-butanedione toluene shows the highest standard deviation with ≈ 22% and ≈ 14%. For that reason hexane as extraction solvent leads to the highest uncertainties of the measurements which is a further hint that hexane is not optimal for the extraction of the oximes. Furthermore dichloromethane shows mostly the best

results regarding the standard deviations of the repeated measurements. Thus this solvent is recommended as the best extraction solvent with the smallest uncertainties.

Minor Corrections

Page 860, Line 23: The deuterated internal standard isn't mentioned in the rest of the article (for example: Page 861, Line 22). It is unclear why/how the internal standard was used.

Authors' comment

The internal standard is used as reference for the GC/MS method. Furthermore during the application of the optimised method for the quantification of the oxidation products methyl glyoxal and 2,3-butanedione the internal standard was used to correct any losses of the analyte that might occur between sampling and detection.

Page 861 Line 22 – 25: The paragraph is changed to *'To improve commonly used PFBHA methods, a mixture of seven standard compounds (acrolein, methacrolein, methyl vinyl ketone, glyoxal, methyl glyoxal, benzaldehyde, 2,3-butanedione) mixed with an internal standard (cyclohexanone-2,2,6,6-d4) was used. The internal standard was used as reference for the GC/MS method or in the case of quantification to correct the peak areas for losses might occur between sampling and detection.'*

The concentration the products methylglyoxal and 2,3-butanedione formed are given (Page 867, Line 10); however, the concentration of 3-methylbutanone isn't mentioned on Page 867 nor in the sample preparation section. The time interval of sampling (1 hour) can be inferred from Figure 2b but isn't mentioned in the text. Can the compounds (A-D) in Figure 2 be differentiated from subsets of the figure (a, b) by more than capitalization?

Authors' comment

The description of the experiment is removed from the supplementary material (Page 1 Line 12-17; S 1.2) to the experimental section in the manuscript. To differentiate the compounds from the subset of the figure methyl glyoxal is abbreviated as "MGly" and 2,3-butanedione is abbreviated as "BuDi" in Figure 2.

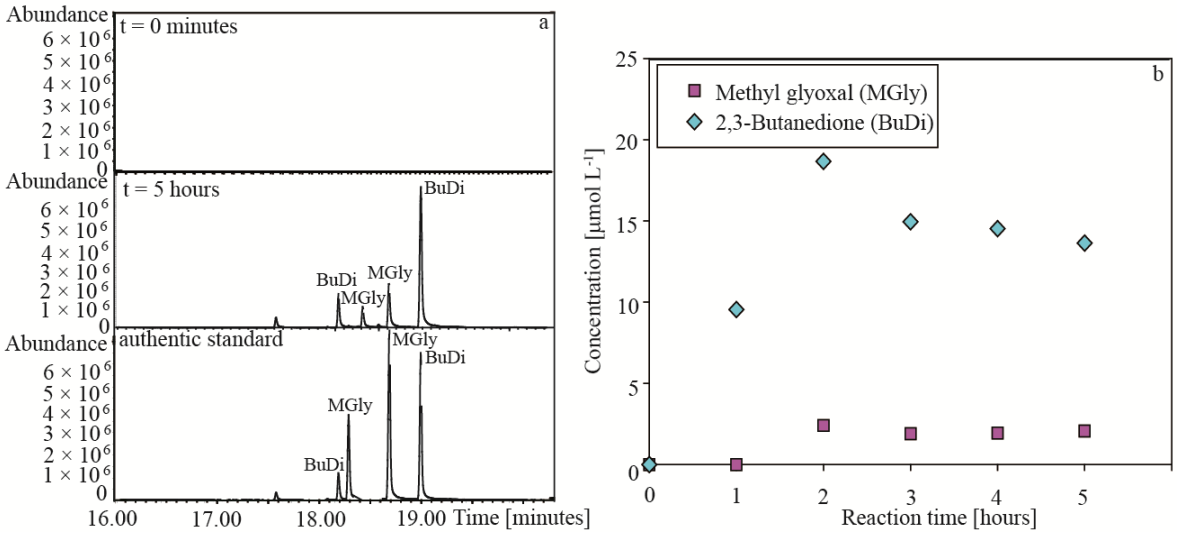

Figure 2. Time-resolved GC/MS chromatograms obtained from the oxidation of 3-metyhlbutanone (starting time t = 0 h and reaction time t = 5 h). For comparison the GC/MS chromatogram of the authentic standard compounds of the identified products 2,3-butanedione (BuDi) and methyl glyoxal (MGly) are shown (a). Using the obtained chromatograms, the concentration of the main products BuDi and MGly was calculated (b).

Page 866, Line 11: What does "SD" refer to?

Authors' comment

The abbreviation SD refers to standard deviation. This was determined by repeating all experiments for three times. The sentence (Page 866 Line 9 – 11) was changed to *'Based on this a pH value of 3 was chosen because this requires no further addition of hydrochloric acid or sodium hydroxide and second, it was found that at pH = 3 the standard deviation (SD, three repetitions) was lower.'*

The sample preparation section (2) provides the optimized times, PFBHA concentration, volumes and pH but not the full range of parameters investigated in the study.

Authors' comment

The authors agree on the reviewer comment, that the parameters optimised during the method optimisation are not mentioned in the experimental section. Only the optimised method is shown. Thus the following sentence is included.

Page 860 Line 26: *'To optimise the PFBHA derivatisation method the influence of the extraction and derivatisation time, the PFBHA amount, the pH value and the extraction solvent was investigated and the measurements were repeated for three times (Table 2). According to the optimal reaction parameters identified 5 mg PFBHA was solved in 1 mL water and 300 µL of the solution was added to the samples reaching a PFBHA concentration of 0.43 mg mL^{-1}.'*

Page 872: The footnotes do not clarify whether all temperatures were approximately 25°C except where noted in column 2.

Authors' comment

Literature studies conducting the derivatisation under room temperature are marked now with an asterisk ('*derivatisation at room temperature').

Table 1: Studies reporting the optimisation of a PFBHA method and fulfil the selection criteria i) derivatise carbonyl compounds in the aqueous phase (derivatisation on solid phase, cartridges or on a chip are not compared: Cullere et al., 2004; Nawrocki et al., 1996; Pang et al., 2013), ii) optimise one of the reaction parameters investigated within this study and iii) use the same extraction techniques as in the present study (solid phase micro extraction or extraction on fibre are not included, e.g. Cancho et al., 2002). The optimised method parameters are given in bold and the parameters matching with the present study are underlined.

PFBHA [mg mL^{-1}]	Derivatisation time	Extraction solvent	Extraction time [min]	Reference
0.1	**40 min, 24 h for ketones***	Ethyl acetate	-	Kobayashi et al. (1980)
0.1	**2 h (longer for ketones)***	Hexane	0.5	Glaze et al. (1989)
> 10 fold excess	**24 h***	Hexan, Methyl *tert*-butyl ether	1	Lelacheur et al. (1993)
0.8	**20 s (900 W)**	Toluene	-	Strassnig et al. (2000)
0.5	24 h*	**Dichloro-methane**	-	Spaulding and Charles (2002)
0.06	**4 h (60°C)**	-	-	Sugaya et al. (2004)
0.2	**24 - 96 h***	Hexane	-	Seaman et al. (2006)
0.06	**2 h***	-	-	Hudson et al. (2007)
-	**4 h***	-	-	Takeuchi et al. (2007)
0.75	**10 min***	-	-	Saison et al. (2009)
0.05	< 10 min*	**Chloro-benzene**	**2**	Ye et al. (2011)
0.5	**1 min (60 °C)**	**Hexane**	1	Serrano et al. (2013)
0.75	2 h (35 °C)	Hexane	3	EPA method 556
0.4	***24 h***	***Dichloro-methane***	***30***	*This work*

Optimised parameters given in **bold**; Matching parameters are underlined; * derivatisation at room temperature

The fifth column has liquid concentrations (possibly aqueous phase) given for some studies and yet what appears to be air volume content for Seaman et al. (2006). There aren't any clarifications of this in the footnotes. Can all the LODs be listed as aqueous extract concentrations so as to simplify the comparisons?

Authors' comment

The detection limits determined by Seaman et al. (2006) are converted from the authors from µg m^{-3} in µmol L^{-1} and listed in Table 3.

The detection limits measured by Seaman et al. (2006) are measured with an electron capture detection (ECD) and thus, they are not comparable.

Thus a footnote "*Concentrations in the gas phase converted from µg m^{-3} to µmol L^{-1}" is included. The sentence (Supplement Page 4 Line 85 – 86; S 2.2) is changed to *'Seaman et al. (2006) determined detection limits with an ECD for acrolein, methacrolein, methyl vinyl ketone, glyoxal, methyl glyoxal and benzaldehyde in the gas phase and not in the aqueous phase. Thus the detection limits have been determined for gas phase measurements and are not comparable to the present method.'*

Page 873: It isn't entirely clear if the table column labeled "repetitions" means replicate experiments and not serial extractions in a single experiment.

Authors' comment

The term "number of repetitions" means that the experiments were repeated for three times. To clarify this a footnote 'Experiments repeated for three times' is included.

Page 874: Table 3 lists "n = 3" in a column heading but isn't clarified in the table footnotes.

Authors' comment

A footnote 'The measurements were conducted with optimal parameters and repeated for three times (n = 3)' is included to clarify 'n = 3'.

Table 3 is missing calculated uncertainty in the detection limit values. There isn't mention of replicates in the sample preparation section (2) and the main paper text is missing uncertainties (such as standard deviation) for LODs and percentages extracted.

Authors' comment

The uncertainty of the detection limits is included as relative standard deviation in the Table and the sentence *'To optimise the PFBHA derivatisation method the influence of the extraction and derivatisation time, the PFBHA amount, the pH value and the extraction solvent was investigated and the measurements were repeated for three times (Table 2).'* is included to mention the repetition of the measurements in the main text.

To show the uncertainties of the detection limits in the manuscript the sentences (Page 862 Line 21 - 25) *'In the case of acrolein this preconcentration results in a detection limit of 0.17 µmol L^{-1} that is improved by a factor of ≈ 2 compared to Glaze et al. (1989). The detection limit of other investigated compounds showed an improvement by about a factor of 10. The detection*

limits were as follows: 0.01± 0.0003µmol L^{-1} for benzaldehyde, 0.01 ± 0.0004 µmol L^{-1} for methyl glyoxal and 0.01 ± 0.0006 µmol L^{-1} for glyoxal (for more details see S2.2 and Table 3). Based on the low standard deviations, it can be stated that the extraction with dichloromethane results in a high reproducibility.

Due to the high reproducibility and low detection limits, dichloromethane was chosen as extraction solvent.'

Table 3: Detection limits of the carbonyl compounds determined in the present study with GC/MS (SIM) and in the literature.

Carbonyl compound	**Detection limits [µmol L^{-1}] in the literature studies**				**This work S/N ≥ 3, n = 3**	
	Glaze et al. (1989)	Seaman et al. (2006)*	Serrano et al. (2013)	EPA method 556	Detection limit ± SD [µmol L^{-1}]	RSD [%]
Acrolein	0.3	$8.6 \times 10^{-3} – 2.5 \times 10^{-2}$	-	-	0.17 ± 0.03	± 19
Methacrolein	-	$4.0 \times 10^{-2} – 1.9 \times 10^{-2}$	-	-	0.02 ± 0.003	± 16
Methyl vinyl ketone	-	$2.2 \times 10^{-2} – 2.9 \times 10^{-2}$	-	-	0.03 ± 0.003	± 10
Benzaldehyde	0.1	$7.5 \times 10^{-3} – 1.7 \times 10^{-2}$	0.1×10^{-3}	0.003	0.01 ± 0.0003	± 3
Glyoxal	0.1	$3.5 \times 10^{-2} – 1.5 \times 10^{-1}$	0.01×10^{-3}	0.01	0.01 ± 0.0006	± 5
Methyl glyoxal	0.1	$1.6 \times 10^{-2} – 2.1 \times 10^{-2}$	0.01×10^{-3}	0.01	0.01 ± 0.0004	± 4
2,3-Butanedione	-	-	-	-	0.01 ± 0.0008	± 8

The measurements were conducted with optimal parameters and repeated for three times (n = 3).

*Concentrations in the gas phase converted from µg m^{-3} to µmol L^{-1};

SD: standard deviation; RSD: relative standard deviation

Page 873: the "Number of repetitions" column has the same value throughout and is perhaps more appropriately removed and mentioned in the table footnotes.

Authors' comment

The column 'Number of repetitions' is deleted and included as a footnote 'Experiments repeated for three times'.

Table 2: Overview about the investigated parameters.

Parameter	Range
Extraction solvent	**Dichloromethane** Toluene Hexane Isooctane Chloroform
Extraction time	5, 15, **30,** 60 min
Derivatisation time	0.5, 1, 2, 6, **24,** 48 h
Added amount of PFBHA	0.09, 0.22, **0.43,** 0.86, 1.72 mg mL^{-1}
pH value (Derivatisation)	pH = 1, **3**, 5, 7
pH value (Extraction)	pH = **1**, 3, 5, 7

Selected parameters given in **bold;**

Experiments repeated for three times.

Page 874: The parameters of the sample preparation are missing from the table footnotes. These were likely the optimal parameters although this isn't specified. Perhaps the significance of the results of this work would be clearer if comparative columns with literature LODs for the seven analytes were added to Table 3 instead of Table 1.

Authors' comment

A footnote "The measurements were conducted with optimal parameters and repeated for three times (n = 3)" to mention the optimal parameters are used to determine the detection limits is included. The detection limits found in the literature were removed from Table 1 to Table 3 for a better comparability of the LOD given in the literature to those determined in the present study.

The sentence (Page 863 Line 17 – 18) is changed to *'These shorter extraction times likely cause significant lower peak areas of the oximes and therefore higher detection limits (Table 3).'*.

The caption of Table 3 is changed to "*Table 3: Detection limits of the carbonyl compounds determined in the present study with GC/MS (SIM) and in the literature.'*

Table 3: Detection limits of the carbonyl compounds determined in the present study with GC/MS (SIM) and in the literature.

Carbonyl compound	Detection limits [µmol L^{-1}] in the literature studies				This work S/N ≥ 3, n = 3	
	Glaze et al. (1989)	Seaman et al. (2006)*	Serrano et al. (2013)	EPA method 556	Detection limit ± SD [µmol L^{-1}]	RSD [%]
Acrolein	0.3	$8.6 \times 10^{-3} – 2.5 \times 10^{-2}$	-	-	0.17 ± 0.03	± 19
Methacrolein	-	$4.0 \times 10^{-2} – 1.9 \times 10^{-2}$	-	-	0.02 ± 0.003	± 16
Methyl vinyl ketone	-	$2.2 \times 10^{-2} – 2.9 \times 10^{-2}$	-	-	0.03 ± 0.003	± 10
Benzaldehyde	0.1	$7.5 \times 10^{-3} – 1.7 \times 10^{-2}$	0.2×10^{-3}	0.003	0.01 ± 0.0003	± 3
Glyoxal	0.1	$3.5 \times 10^{-2} – 1.5 \times 10^{-1}$	0.02×10^{-3}	0.01	0.01 ± 0.0006	± 5
Methyl glyoxal	0.1	$1.6 \times 10^{-2} – 2.1 \times 10^{-2}$	0.01×10^{-3}	0.01	0.01 ± 0.0004	± 4
2,3-Butanedione	-	-	-	-	0.01 ± 0.0008	± 8

The measurements were conducted with optimal parameters and repeated for three times (n = 3).

*Concentrations in the gas phase converted from µg m^{-3} to µmol L^{-1};

SD: standard deviation; RSD: relative standard deviation

Page 859, Line 04: it appears that “depending” implies a scale or range which isn’t discussed thereafter.

Authors’ comment

The sentence is changed to *‘According to their Henry constants carbonyl compounds partition into the aqueous phase and due to their high solubility in water they can undergo multiphase reactions (Ravishankara, 1997; Schaefer et al., 2012).’*

Page 863, Line 10: “repeated three times” appears to refer to serial extractions of a single solution. The percentage un-extracted analytes remaining is given for the 2nd extraction but not for the 1st or 3rd extraction.

Authors’ comment

The extraction was repeated for three times for one sample solution to determine the extraction efficiency. After the first extraction only ≈ 2% of the carbonyl compounds were found in the solution. This means the first extraction has an extraction efficiency of ≈ 98%. The second extraction leads to a complete extraction or in other words to a concentration of the carbonyl compounds smaller than the detection limit. Thus no carbonyl compounds can be found in the third extraction solution.

The sentence (Page 863 Line 10 – 12) was changed to ‘*After the first extraction the amount of detected oxime was negligibly small (≈ 2 %, Table S 2; Supplement S2.3) indicating an almost*

complete extraction within 30 min e.g., methyl vinyl ketone, benzaldehyde and methyl glyoxal showed an extraction efficiency of 98 % ± 2 % after the first extraction.'

There are a few sentences lacking commas between phrases and ideas which may detract from the coherence of the material (page 861, lines 10 and 22, following "compounds" and "methods" respectively; page 864, line 27 following "formed").

Authors' comment

The manuscript was carefully edited and missing commas were added.

Page 861 Line 22 – 25: The sentence is changed to *'To improve commonly used PFBHA methods, a mixture of seven standard compounds (acrolein, methacrolein, methyl vinyl ketone, glyoxal, methyl glyoxal, benzaldehyde, 2,3-butanedione) mixed with an internal standard was used.'*

Page 864 Line 26 – Page 865 Line 1: The sentence is changed to *'After the carbonyl-bisulfite adduct was formed, hydrogen peroxide was added to destroy the formed adduct and to yield carbonyl compounds which were directly derivatised with PFBHA.'*