

Interactive comment on “Characterisation and optimisation of a method for the detection and quantification of atmospherically relevant carbonyl compounds in aqueous medium” by M. Rodigast et al.

Anonymous Referee #3

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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.

1 Major Corrections

Sections 3.1 – 3.4: There are multiple positive and negative effects determined by
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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. Are the times listed on Line 4 for just the seven target compounds of this study? Are the magnitudes of each of the positive and negative effects on LOD the same for each parameter optimized in this study? Can the comparisons be clarified?

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?

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.

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”? 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?

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.

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?

2 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.

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?

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

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.

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

Page 873: It isn't entirely clear if the table column labeled "repetitions" means replicate experiments and not serial extractions in a single experiment. Page 874: Table 3 lists "n = 3" in a column heading but isn't clarified in the table footnotes. 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. Page 873: the "Number of repetitions" column has the same value throughout and is perhaps more

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appropriately removed and mentioned in the table footnotes.

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.

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

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.

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").

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