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Atmospheric Measurement Techniques
Discussions

Interactive comment on "Organic and inorganic decomposition products from the thermal desorption of atmospheric particles" *by* B. J. Williams et al.

B. J. Williams et al.

brentw@wustl.edu

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*A revised document (with Track Changes enabled) as well as corrected figures and supplemental figures has been provided to the editor.

Anonymous Referee #2

General Comments:

The manuscript of Williams et al. investigates the thermal decomposition products which are formed due to thermal desorption of aerosol samples in the CTD cell of the thermal desorption aerosol gas chromatograph (TAG) instrument. Specifically Williams et al. investigate the usually omitted first section of the GC chromatogram (the “solvent delay”) where the ion signals of the thermally unstable fragments which pass unretained through the column are detectable. A detailed analysis of typical mass fragments for inorganic and organic tracer ions of the “decomposition window” is given for a set of calibrations and two field studies. Additionally the TAG field study results are also compared with results obtained from a co-located AMS using the same ions for inorganic and organic fragments which are well established in the AMS community to represent mass loadings of nitrate, sulfate, ammonium, and organics in the aerosol. The manuscript is well written and explores a new set of analysis techniques which shows that also the non-resolved signals in the GC chromatogram of the TAG instrument contains significant and important information. These analysis techniques show potential to be used to quantify thermally instable inorganic and organic components of aerosols which rely on desorption techniques.

I recommend publication in AMT after addressing some minor comments mainly addressing clarifications in the text and figure display.

Author Response: The authors thank the reviewer for their comments and address further questions below.

Specific Comments:

1) p. 16, l. 17ff: It would be instructive to mention if and how much carryover was also observed in the case of injecting calibration compounds. It might help to understand better if carryover is due to not long enough heating time or e.g. maybe the organic matrix in the ambient aerosol versus the pure inorganic compounds injected.

Author Response: Although limited inorganic standard testing was performed, it was observed that only 3% of the signal (m/z 30) remained in a second desorption for the ammonium nitrate standard and 30% of the signal (m/z 64) remained in a second desorption for ammonium sulfate. This is on the order of the carryover observed above baseline in ambient sampling (Fig. 4e, 4g). The aerosol mixture does not appear to greatly impact the completeness of desorption/decomposition. Text has been added to incorporate this observation:

“The extent of carryover of nitrate and sulfate from sample to sample was similar for pure calibration standards as was observed above baseline in ambient sampling (from Fig. 4e,g). It was observed that only 3% of the signal (m/z 30) remained in a second desorption for the ammonium nitrate standard and 30% of the signal (m/z 64) remained in a second desorption for ammonium sulfate. The aerosol mixture does not appear to greatly impact the completeness of desorption/decomposition for these components.”

2) p. 18, l. 13: “Since there is no subtraction of background (cell blank). . .” I have trouble understanding this sentence and it would be beneficial to split it up in more sentences. I have the impression that too much information is squeezed into one sentence. It is said that there is no subtraction of the background (no cell blanks) signal. Does this mean no gas phase background to subtract due to the use of the gas phase denuder? Couldn’t there be any particle residue background which needs to be subtracted using subsequent cell blanks? What is the “additional” subtraction; additional to what? How often were the “additional” cell blanks acquired? Was the average percentage of cell blank signal obtained for the whole 16 min region?

Author Response: The following text has been altered to improve clarity for this section:

“In using the denuded ambient data as particle-only signal, it is required to incorporate background (cell blank) signal subtraction. This subtraction was accounted for in the previously discussed filtered/ambient time periods since the background was present in both signals, and therefore subtracted out when acquiring particle-only signal. When using denuded data, background subtraction is accounted for by acquiring regular cell blanks, interpolating cell blanks onto denuded time line, determining an average percentage of cell blank signal compared to denuded sample signal, and finally subtracting this fraction from each denuded sample.”

And. . .

“Identical ion integration methods were applied for each sample type (filtered, ambient, denuded, cell blanks) across the entire decomposition window.”

3) Figure 4e) to 4g) It is confusing to read the graphs if the right and left y-axis have different ranges. E.g. 4e) m/z48 as lower values than m/z64 which would be clearly visible if both y-axis have the same range. Especially true for 4g) and 4h) which indicates the opposite behavior of m/z30 to m/z 46, and m/z53 to m/z82, respectively, by looking at the graph.

Author Response: It is most important in these figures (4e-h) to observe the relative changes for each ion from the first (ambient) sample. The absolute scale is of minor importance for the points being made, and therefore we fix the first (ambient) sample response to max scale (on each axis) and apply different scales for primary and secondary y-axes to show the relative changes throughout subsequent analyses. Shown this way, we can see that m/z 44 and m/z 46 have relatively elevated background signals compared to other ions, and we see that the pairs (m/z 53+82 and m/z 64+48) have identical trends. These plots are similar to having normalized to the first sample, except the absolute signal is still reported on the axis if of interest. For these reasons, we would prefer to keep figures 4e-h in their current state.

4) Figure 5a) and 5b) Was the injection of each concentration repeated? If so how often? It is especially for calibration correlations informative to have error bars for each data point. Please add the error bars to the graphs.

Author Response: Unfortunately we were not able to repeat injections due to the coating damage experienced during the initial injections. A statement to clarify this has been added.

“Unfortunately, due to damage from pure component standards, we were not able to perform repeat injections of these standards to incorporate uncertainty estimates in Fig. 5, and therefore, these calibrations are not used to report actual mass concentrations at this point in development.”

5) Figure S3c: The legend is obscured by the graph.

Author Response: I think this comment is in regards to Figure S4c. Figure has been recreated so legend is visible.

6) Figure S4: The run numbers are not very informative. The date for each sample could be put better into context e.g. with graph S5).

Author Response: Good point. Run numbers have been changed to dates in altered Figure S4.

Interactive comment on Atmos. Meas. Tech. Discuss., 8, 13377, 2015.

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Interactive Discussion

Discussion Paper