

# Fragment ion-functional group relationships in organic aerosols using aerosol mass spectrometry and mid-infrared spectroscopy”

## Reviewer 1

This article presents a comparison of chamber SOA interrogated with IR spectroscopy and aerosol mass spectrometry, in an effort to use the strengths of each to build something greater than the sum of its parts. The key drawbacks to each approach (temporal resolution for IR spectroscopy and functional group accuracy for mass spec) are clear, and the authors have taken advantage of a multi-variate regression and other analytical techniques to bridge the obvious gaps in the data each method presents. This makes the article both relevant and novel, and the use of their multi-variate approach is novel as well. Further, mechanisms of aging can be interrogated by the comparison of these two methods - that is, there is value in their differences as well. The authors have certainly achieved this goal, and have communicated the results fairly clearly.

The results indicate a potential for this approach to provide greater insight in future studies as well as some words of caution about using tracer fragments from AMS. These conclusions are well-supported by the data they present as well as the references cited.

Further Reviewer Questions:

Are substantial conclusions reached? Yes

Are the scientific methods and assumptions valid and clearly outlined? Yes, clearly so.

Are the results sufficient to support the interpretations and conclusions? Yes.

Is the description of experiments and calculations sufficiently complete and precise to allow their reproduction by fellow scientists (traceability of results)? Yes, very clear descriptions are provided.

Do the authors give proper credit to related work and clearly indicate their own new/original contribution? Yes.

Does the title clearly reflect the contents of the paper? Yes.

Does the abstract provide a concise and complete summary? Yes.

Is the overall presentation well structured and clear? Yes.

Is the language fluent and precise? Yes.

Are mathematical formulae, symbols, abbreviations, and units correctly defined and used? Yes.

Should any parts of the paper (text, formulae, figures, tables) be clarified, reduced, combined, or eliminated? I have made small suggestions above.

Are the number and quality of references appropriate? Yes.

Is the amount and quality of supplementary material appropriate? Yes.

[We thank the reviewer for the encouraging review of the manuscript.](#)

## General comments

1. One small criticism is the readability of the manuscript, and I provide some very minor suggestions to improve this. The nature of this work is that the results are tedious to report, so this is not a major criticism. Overall, the paper is suitable for publication with some minor improvements.

The manuscript was made more readable by omitting unnecessary sentences and acronyms.

## Specific comments

2. Section 3.1.3 (but possibly earlier) - the authors are using CC for coal combustion and WB for wood burning. It took me quite some time to internalize those acronyms while reading the analysis, where many other acronyms are used. Because they are not very commonly used acronyms (unlike SOA or OM), it adds confusion to use these instead of the full terms. I appreciate that the terms are used many times in the analysis, and that spelling out the phrases will make for longer sentences. However, I would have to read the paper at least twice to be comfortable with them. I leave it to the authors to decide how to proceed on this point, but I felt it was worth sharing. Given how dense the manuscript is, having uncommon acronyms interfered with my ability to process the information.

In the revised version, CC, WB, FG, and naCO acronyms were replaced by their corresponding phrases to help the readability.

Likewise, when using naCO (as in line 295), it would be very helpful to have “non-acid carbonyl” written as well.

The term “non-acid carbonyl” was added to help the readability.

3. Line 296 - It appears that the offset between AMS and MIR in estimated H:C is in the opposite direction for wood burning and coal combustion particles. It is worth the authors pointing this out to readers, and perhaps speculating on why this might be. A different offset, but in the same direction, is easier to understand than a similar magnitude offset in the opposite direction.

The positive offset for the wood burning aerosols (higher H:C of FTIR compared to AMS) might be due to the uncharacterized C from aromatic rings of lignin pyrolysis products, leading in to an overestimation of H:C. The latter was clarified in the revised manuscript. In addition, in order to be able to convert functional group abundances to elemental ratios, it is assumed that each alcohol or aliphatic CH function group contains 0.5 C (like straight-chain alkanes or alkanols) (Maria et al., 2002; Reggente et al., 2019b). This assumption is dependent on the structure of the molecules and might not be always accurate.

The following sentences were added to the revised manuscript:

**The positive H:C offset for the wood burning aerosols might be due to the uncharacterized carbon from aromatic rings of lignin pyrolysis products, which can lead to an overestimation of H:C.**

**The discrepancies between the measurements of the two instruments might stem from the low OM mass collected on the filters, which increases the baseline correction and peak fitting uncertainties in MIR analysis. The existence of functional groups that are not considered in the peak fitting algorithm (e.g., ethers, PAHs, rC=C and rCH), and the assumption about the fractional carbon associated with each functional group might also play a role. Sampling biases of semi-volatile compounds on PTFE filters (Subramanian et al., 2004) and the uncertainties of AMS**

**elemental ratio calibrations (Canagaratna et al., 2015; Aiken et al., 2008) can also affect the results.**

4. Table 1 would be more readable if functional groups had their names.

The names of functional groups were added to the table in the revised version.

5. Line 272 (discussion of Figures 4a and 4b) - I was not sure, until much later, that 4a and 4b represent replicate experiments, and not experiments with slightly different conditions. This became clear at the very end of the manuscript. It would be useful to note this in the caption for Figure 4 as well as in the text (especially since there are varying numbers of replicate results for each combination presented in Figure 4).

We clarified in the Methods section and the figure's caption that there are one to three similar experiments of each category.

6. Figure 5 has two similar shades of green used for COOH and naCO and it is very challenging to distinguish them. Similar for Figure 6 and Figure 8.

The color scheme used in the manuscript is the one commonly used by the FTIR community (e.g., Gilardoni et al., 2009; Takahama et al., 2011; Reggente et al., 2019b; Bürki et al., 2020; Yazdani et al., 2021). Thus, it was not changed for the sake of consistency. However, to aid readability, important mass fragments for each functional group have also been highlighted in the figure in the revised figures.

7. Line 382 - Are the authors referring to the normal subtraction of gas phase mass spectra in "compensation" or some special treatment of the data?

The term "compensation" was changed to "subtraction" to avoid confusion. We refer to the elimination of the interference from gas-phase species in the  $\text{CHO}^+$  and  $\text{CO}_2^+$  signals. In particular, the  $\text{j}_{15}\text{NN}$  isotope and the gas-phase  $\text{CO}_2$  interfere with  $\text{CHO}^+$  and  $\text{CO}_2^+$ , respectively. Their concentration is often inferred from the concentration of  $\text{N}_2$  ([http://cires1.colorado.edu/jimenez-group/wiki/index.php/Main\\_Page#ToF-AMS](http://cires1.colorado.edu/jimenez-group/wiki/index.php/Main_Page#ToF-AMS)). The subtraction is implemented in Pika. We show here that the subtraction works effectively although the interference is significant especially for  $\text{CHO}^+$ .

8. Line 390 - The authors note that different aerosol source will benefit from different fragments being used as tracers for (for example) alkane. Do the authors have suggestions or are they simply commenting that this fragment was not the expected one, or maybe one that is not commonly used in other studies, but was the winner for the VIP analysis?

Our understanding is that when comparing alkane between different sources, small fragments such as  $\text{C}_3\text{H}_5^+$  are better correlated with the abundance of the alkane CH group compared to the larger, more common fragments like  $\text{C}_4\text{H}_9^+$  and  $\text{C}_5\text{H}_{11}^+$ . On the other hand, when considering OM from coal combustion relatively large fragments ( $\text{C}>10$ ) appear to be highly correlated with the alkane CH.

This sentence of added in the revised version:

**For example, in this study, the  $\text{C}_3\text{H}_5^+$  fragment appears to be more correlated with the aCH group than the commonly used fragment,  $\text{C}_4\text{H}_9^+$ .**

#### Technical corrections

9. Figure is missing the y-axis label.

The label was added to the figure.

10. Line 277 - the sentence would read better if "low" and "lower" became "small" and "smaller"

“Low” and “lower” were substituted by “small” and “smaller”.

11. Line 290 - The sentence “The high H:C ratios before aging support the low amount of aromatics to aliphatic CH observed from MIR spectra” is awkward. I suggest, “The high H:C ratios before aging are consistent with the high ratio of aliphatic CH to aromatic carbon observed in MIR spectra.”

The sentence was replaced by the suggested one.

12. Line 343 - insert “also” before “known” to read “fragment is also known”

The word “also” was added.

13. Line 383 - is “carbonyl CO” the same thing as  $\text{NaCO}$ ?

Since we are referring to the carbonyl peak, it can be both due to non-acid or acid carbonyls (there is only a small frequency difference between the two). However the absence of the broad acid OH peak suggests that the carbonyl peak is predominantly due to non-acid carbonyl. This was clarified in the manuscript.

## Reviewer 2

The manuscript “Fragment ion-functional group relationships in organic aerosols using aerosol mass spectrometry and mid-infrared spectroscopy” presents an attempt to combine two methods, aerosol mass spectrometry (AMS) and mid-range spectroscopy, to extract information and gain further insight into the composition of organic aerosols, especially regarding functional group information.

Information from the Aerodyne AMS with its very good temporal resolution but strong fragmentation due to thermal desorption and subsequently electron ionization is combined with mid-infrared spectroscopy with low temporal resolution but very detailed analysis of the functional groups of the analyzed organic aerosol. Together with the thorough mathematical framework presented by the authors this results in very detailed profiles of the temporal evolution of the analyzed organic aerosol.

Thus, the study presented by the authors is a very important contribution and justifies publication after some minor changes and corrections.

We thank the reviewer for the encouraging assessment.

1. The manuscript could benefit from a small revision regarding readability due to the large number of used abbreviations and acronyms, wrong punctuation, and unnecessary filler words.

The number of acronyms was reduced. In the revised manuscript, wood burning, coal combustion, functional group, and non-acid carbonyl are used instead of their acronyms (WB, CC, FG, and naCO). The manuscript was revised with regard to punctuations and filler words were reduced.

2. Another general point are the concluding remarks. These are quite short for such a long manuscript with important results which could prove quite useful for the AMS community. A more conclusive summary of the manuscript would be very helpful for the audience.

The conclusion was made longer and more conclusive. The new conclusion reads as follows:

**We combined statistically collocated AMS and MIR measurements in an environmental simulation chamber and found that AMS OM is associated the most with aCH, aCOH, COOH, and non-acid carbonyl (naCO) functional groups for aerosols generated from the combustion of wood and coal. The OM mass, OM:OC, H:C, and O:C estimated from the abundances of the mentioned functional groups were in good agreement with those from AMS measurements and showed clear variations across fuel types and oxidants. These functional groups are those that were used in previous studies of atmospheric aerosols using MIR (e.g., Maria et al., 2003; Russell et al., 2009b; Reggente et al., 2019a).**

Previous studies of functional group-ion fragment relationships were limited to small fragments and did not consider marker signatures in the mid-infrared spectra (Russell et al., 2009a; Faber et al., 2017). We performed a univariate (correlation and covariance) analysis on the four mentioned functional groups and more than 300 fragment ions up to  $m/z$  212 in the AMS spectra and found several small (low  $m/z$ ) and large ( $m/z > 100$ ) AMS fragment ions to be informative about the functional group composition of POA and SOA from the combustion sources. For example,  $C_7H_6O_4^+$ , which was only detected in wood burning SOA and was highly correlated with the COOH functional group, might be used as a potential marker of biomass burning SOA in the atmosphere. The peaks in the FTIR spectra that were believed to be associated with biomass burning markers (levoglucosan and

lignin-like compounds) were also found to be highly correlated with the fragments related these markers.

Our multivariate (VIP scores) analysis indicated that when OMs with different proportions of oxygenated functional groups (i.e., COOH, aCOH, and naCO) are fragmented in the AMS, they produce different proportions of the major oxygenated fragments (i.e., CO<sub>2</sub><sup>+</sup>, CHO<sup>+</sup>, C<sub>2</sub>H<sub>3</sub>O<sup>+</sup>). For examples, C<sub>2</sub>H<sub>3</sub>O<sup>+</sup> was found to be associated the most with non-acid carbonyl and SOA species formed with nitrate radical. However, each of these small oxygenated fragments does not represent only a single functional group and contribution from other functional groups is expected.

Finally, we developed a method to extract the high-time-resolution functional group information from the AMS spectra to better understand the evolution of the OM composition during the course of aging. The results of this method provide insights into the oxidation pathways that cannot be independently obtained from the van Krevelen plot. The results of this method, which can be easily implemented in other environmental chamber studies, suggest the formation of moderately oxygenated functional groups (e.g., non-acid carbonyl) soon after the start of aging and the transformation of moderately oxygenated functional groups to more oxygenated functional groups (e.g., acid) with continued aging.

3. One last general remark (respectively question): while title suggests that the manuscript deals with organic aerosols in general, the experiments conducted by the authors are all combustion related. Can the developed methods and comparisons be applied to other types of organic aerosols (e.g., SOA from VOC precursors), or did the authors already try this?

We have also tried the methods (e.g., VIP scores method) in another series of environmental chamber experiments with different a biomass fuel (pellet, manuscript in preparation) and obtained similar results regarding the relationship of functional groups and fragments ions; more studies over a wide range of organic aerosol types can better constrain our interpretation regarding the functional groups represented by each mass fragment. We believe that the method for obtaining high-time-resolution functional groups is applicable to emissions from other types of fuels and organic aerosols from single VOC precursors. The method is easy to implement and can be tested on different chamber datasets to gain additional insight into the evolution of OM.

#### **Specific comments and technical corrections:**

4. L32: In which way are these functional groups influential to AMS OM?

The VIP scores method determines the functional groups that are associated the most with the AMS OM or in other words functional groups that are the best predictors of AMS OM. This was clarified in the Methods section.

5. L58: I believe “electron ionization” is the correct term for the ionization method used by the Aerodyne AMS.

The term “electron impact ionization” was replaced by “electron ionization”.

6. L172: Should be “[...] show the production of fragments from FGs”. Same in L177, the fragment ions are not produced by the functional groups!

The statement was substituted by:

**[...] as they do not show the production of fragments from molecules containing the functional group of interest.**

7. L176: I recommend using “small” instead of “light”.

In the revised manuscript, “light” and “heavy” were substituted by “small” and “large”.

8. L191: Please rephrase this sentence: “Thereafter, the high-resolution O:C ratios separated [...] were calculated from the high-resolution resolution FG compositions [...]”.

The rephrased sentence reads as follows:

**The contribution of oxygenated functional groups to the bulk O:C ratio was calculated from their high-time-resolution abundances.**

9. L265: Should be “[...] which is reflected [...]”.

The sentence was corrected based on the suggestion:

**[...] resulting in a different SOA composition, which is also reflected in both AMS and MIR measurements.**

10. L266: What is a “local slope”? Please rephrase.

We meant to distinguish between the average slope of the curve and the slope of the tangent line at each point. The term “local slope” was substituted by “slope”.

11. L270: Could there be other reasons for the bend in the van Krevelen aging trajectories (e.g., wall losses)? Where the mass concentrations similar for all those experiments?

There are some variations in the mass concentration across the experiments. SOA, however, dominates the composition of aerosols in the majority of experiments after aging. Please refer to Yazdani et al. (2021) for details. Based on SMPS data, aerosols are expected to be internally mixed. As a result, losses to the chamber walls have negligible effect on the aerosol composition. The chemical aging, on the other hand, probably has the dominant effect on the chemical composition and the van Krevelen slopes.

We have already observed (unpublished data) that wall losses alone have insignificant effect on the composition of aerosols in the chamber and only change the concentration of OM.

12. L309 (also L311, L322): I recommend using “large” instead of “heavy”.

In the revised manuscript, “light” and “heavy” were substituted by “small” and “large”.

13. L310: “[...] these aerosols is [...]” should be “[...] these aerosols are [...]”.

The sentence was corrected

14. L310-L311: What are “relatively longer chain hydrocarbons”? Relative to what?

That statement has been made relative to wood burning aerosols. The sentence was clarified in the revised version.

15. P15, Fig. 5: The chemical composition? of the individual fragments in the plot is illegible and superfluous since all the important fragments are labeled. The same applies to Fig. 6.

The chemical formulas were omitted from the figures in the revised version.

16. L462: Again, I recommend to use “small” and “large” instead of “light” and “heavy”.

In the revised manuscript, “light” and “heavy” were substituted by “small” and “large”.

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