

## ***Interactive comment on “Elemental analysis of chamber organic aerosol using an aerodyne high-resolution aerosol mass spectrometer” by P. S. Chhabra et al.***

### **Anonymous Referee #1**

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#### General Comments:

In this manuscript, Chhabra et al. examine the elemental ratios of secondary organic aerosol (SOA) formed from a series of chamber reactions under different conditions using data obtained from a high-resolution time-of-flight aerosol mass spectrometer (AMS). Obtained elemental analysis results are compared with those obtained from offline analysis of comparable chamber SOA and also with results of AMS elemental analysis of ambient organic aerosol (OA) in order to gain additional insight into the chemical composition and potential sources of ambient OA. Overall, elemental analysis of chamber SOA in the current study were similar to those obtained using offline

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techniques further highlighting the robust nature of the AMS elemental analysis technique. The degree of oxidation of SOA formed in the majority of investigated systems (as measured by the O/C ratio), however, is lower than those of the most highly oxidized OA components identified from ambient OA by positive matrix factorization. As pointed out by the authors, this emphasizes the need for longer scale chamber experiments to adequately replicate the degree of oxidation experienced under ambient conditions.

Overall, the manuscript is well written and thoroughly referenced and worthy of publication in Atmospheric Chemistry and Physics.

Specific Comments:

1. In the last sentence of the abstract, a reference is made to PMF components without explicitly stating that this refers to components of ambient OA obtained from PMF analysis.
2. In the experimental section (2.2 specifically), the authors detail the sampling mode of the AMS during the chamber reactions and state the AMS mode was switched every minute between the high resolution "W-mode" and the higher sensitivity "V-mode". W-mode data was used for the elemental analysis results while the O/C ratio was estimated as the fraction of m/z 44 to total organic signal using V-mode data. Calculated O/C ratios and estimated O/C were later compared to evaluate whether the ratio of m/z 44 to total organic signal was an adequate estimate of O/C for chamber reactions. I am curious as to why V-mode data was used to estimate O/C ratios instead of applying the same fragmentation tables to the W-mode data which was the basis of the elemental analysis as it would lead to a more direct comparison of the two metrics (e.g., tuning differences between the two modes would have no impact, etc.).
3. At page 27493, line 10, the authors discuss the correction for CO<sub>2</sub><sup>+</sup> needed to remove the contribution from air. However, the authors end this sentence by stating that the air contribution to CO<sub>2</sub><sup>+</sup> is removed to "determine the organic signal at m/z 44". It would be more correct to state that this determines the organic signal at CO<sub>2</sub><sup>+</sup>

as there are additional organic fragments at nominal  $m/z$  44 including  $C_2H_4O^+$  as evidenced by Figure 5A.

4. On page 27497, the authors compare elemental analysis values obtained using AMS data for alpha-pinene ozonolysis with those calculated using the offline analysis results of Yu et al. (1999). Although the elemental ratios obtained from each measurement are similar, there is some question whether this is merely coincidental as the AMS and off-line analyses would not measure the same species due to the labile nature of many of the SOA constituents in this case. For example, Yu et al. (1999) claim that > 90% of SOA resulting from the ozonolysis of alpha-pinene is contributed by compounds containing carbonyl, hydroxyl, and carboxyl groups. However, using an iodometric-spectrophotometric technique, Docherty et al. (2005) found that nearly half of the SOA mass from this reaction consists of organic peroxides. These results were supported by additional experiments conducted by Surratt et al. (2006). These compounds would not likely be amenable to gas chromatography and may decompose to the products measured by Yu et al. The potential for this discrepancy should, at a minimum, be discussed in section 4.3 where other potential sources of uncertainty regarding offline analytical techniques are discussed.

5. Combining Tables 1 and 2 should be considered so that elemental analysis results can be reported for each replicate reaction. This would clearly show the range of O/C ratios which are depicted in Figure 16. Again considering Table 2, this table claims to provide the average ratio for each experiment. The O/C range for the four alpha-pinene + O<sub>3</sub> reactions is 0.30-0.43, but the average is 0.43. How can that be? Please recheck these numbers.

Technical Corrections:

Page 27487, line 21: the range of O/C ratios provided is incorrect (0.010 should be 0.10).

Page 27490, line 7: incorrect units for volume concentration ( $m^3\ cm^{-3}$  should be  $cm^3$ )

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m-3).

Page 27491, line 24: the abbreviation HR-MS was never introduced and is unnecessary as it is only used once in the manuscript. I would suggest simply using "high-resolution mass spectra".

Page 27492, line 15: "by" or "in" should follow "described".

Page 27492, line 21: "HR-AMS" abbreviation is used to refer to the high-resolution time-of-flight aerosol mass spectrometer when the abbreviation "AMS" was introduced at page 27491, line 12. Please correct.

Page 27503, lines 1-4: The first sentence here is a fragment and may need to be combined with the second. Please revise.

Page 27505, line 5: Comma following "chemical bond" should be removed.

Page 27505, line 28: "that" appears to be a typo and should be "than".

Page 27507, line 23: Sentence reads " monomers measured detected through..." Remove either "measured" or "detected".

Page 27508, line 16: "oligioesters" is misspelled.

Page 27509, line 8: omit "in" after "sulfonic".

Page 27510, lines 1-5: Sentence beginning "It is likely..." is a fragment. Please revise.

Page 27510, line 29: Comma following m/z 44 is unnecessary.

Table 3: "This Study" for toluene + OH should be bold to be consistent.

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