

## Referee #2

*This manuscript (amt-2018-17) reports an approach that couples the Aerosol Mass Spectrometer (AMS) to a volatility and hygroscopicity tandem differential mobility analyser (VH-TDMA) setup. This approach allows separation of the semi-volatile and low volatility components and comparison to chemical composition. The main novel advance of this approach over other similar approaches is the incorporation of size dependent aerosol chemical composition from the AMS, which allows investigation of aerosol chemical composition in the size range most relevant to the VH-TDMA experiments and to cloud droplet activation. The manuscript is well written and within the scope of Atmospheric Measurement Techniques. The manuscript may be publishable if the below major comments associated with data quality and the use of the thermodenuder are addressed in revision.*

### Author

The authors appreciate the reviewer's comments that have helped us to refine the manuscript. We have implemented several changes to our analysis which have significantly improved the quality of the data and subsequent derived findings. The manuscript has been updated with a detailed discussion of this revised analysis, particularly in Sections 2.3, 2.6 and 3.1.

Responses to the reviewer's comments have been included below. Please note that text coloured in **red** refers to the added text in the manuscript. All page and line numbers refer to the revised manuscript (Revised\_Manuscript\_TrackedChanges.docx) and supplementary material (Supplement.docx) where all changes have been tracked. If the text has been significantly changed, only the section number is given in this document (e.g. "**Section 2.5**").

### **Major comments**

#### Referee's comment

*1. The first major comment relates to data quality and echoes many of the comments from Anonymous Reviewer 1. The authors assert that the main advantage of their approach over previous similar approaches is the incorporation of size dependent aerosol chemical composition measurements. However, the authors also state that, for the chamber measurements, which had a much higher mass concentration than the ambient measurements, "the observed signal was quite unstable...often falling below the detection limit. For this reason, data below the detection limit was not removed as it would have excluded a large proportion of the data" (page 7, lines 13-15). If the signal is so unstable and a meaningful measurement so difficult to obtain, it is unclear how this approach represents an advance over previous versions, which is the key argument of the paper. The robustness of this approach must be discussed in substantial detail in any revision. Included in that discussion must be details concerning the experiments (e.g. whether the AMS measurements in Fig. 3 represent the fraction around 100 nm in the smog chamber and, if not, what the mass concentrations around 100 nm were during that experiment; what time resolution was used in the AMS measurements and how that compares to the time dependent composition changes; what is, and what factors are governing, the AMS limit of detection; what mass concentrations are required for this approach to be viable; etc.).*

### Author's answer

1. The authors hope that the changes made in response to Anonymous Reviewer 1's comments will address many of the concerns regarding data quality. In short, by averaging the AMS measurements of chamber-generated SOA to a lower time resolution, both the detection limits and the variability of most species were substantially improved. As a result, it was no longer necessary to artificially smooth the data.  $\text{NH}_4$  was an exception, as its AMS signal is commonly less stable than other species and was more strongly affected by the reduced signal to noise ratio offered by PTOF measurements. Since  $\text{NH}_4$  contributes a significant fraction of AS mass, it could not be excluded from the analysis, however it was necessary to reduce its variability by estimating  $\text{NH}_4$  concentrations using a simple linear fit to the  $\text{NH}_4$  PTOF data. The resulting composition-based HGF models still obtain close agreement with the direct VH-TDMA measurements, so we are confident that this methodology offers meaningful results even when sampling rapidly changing, size-dependent aerosol. [Section 3.1](#) has been substantially rewritten to discuss the revised analysis and results from this experiment. We would like to also directly respond to the specific concerns mentioned in the referee's comment.

### **Mass concentrations at 100 nm:**

Fig 3a (now renumbered as [Fig 4](#)) represents the bulk mass concentrations of non-refractory species. The caption and corresponding text has been reworded to clarify this. A new figure has been added to the supplement ([Fig S3](#)) which gives the heated and unheated mass concentrations for aerosol at 100 nm

### **AMS time resolution**

As mentioned on P3 L17, the combined system typically samples with a time resolution of 3 minutes per sample (6 minutes per unheated/heated cycle). This time resolution was halved for the chamber experiment to obtain satisfactory signal averaging while being fast enough to observe trends in the composition during SOA formation (discussed on P7 L14).

### **AMS limit of detection**

A brief discussion of AMS detection limits and uncertainties has been added to [Section 2.1](#) (P2, L33). Further discussion regarding the sensitivity of AMS measurements, and limitations of using PTOF measurements has been included in [Section 3.1](#) (P7, L9),

### **Required mass concentrations**

We have not attempted to estimate necessary mass concentrations for this approach, because it is situational. In essence, there needs to be a balance between the required time resolution, size resolution and available mass concentration. For example, mass concentrations were very low during the Cape Grim experiment, however meaningful observations were still possible by analyzing bulk aerosol measurements and using a low time resolution.

### Referee's comment

*2. The second major comment relates to the use of the thermodenuder approach. It is known that many chemical components of secondary organic aerosol (e.g. oligomers) can thermally decompose when passed through a thermodenuder at temperatures as low as 100°C (Hall and Johnston, *Aerosol Sci. Technol.*, **2012**, 46, 983-989). This observation may have a significant impact on the interpretation of the VHTDMA measurements, especially since the thermodenuder used in this manuscript is ramped up to 500°C. In the revised manuscript, the authors should include a discussion of the limitations of the thermodenuder approach with respect to separation of semi-volatile and low volatility components against likely changes to*

*aerosol chemical composition resulting from thermal decomposition within the thermodenuder.*

Author's answer

2. The potential for chemical change due to heating is an important underlying consideration which affects many thermal sampling processes. We appreciate the inclusion of the study by Hall and Johnson, and have added this limitation to the discussion of volatility-based sampling in **Section 2.2**.

**Minor comments**

Referee's comment

*1. In their revised manuscript, the authors need to better clarify the temperature threshold that separates semi-volatile from low volatility. Is the cut-off at 120°C? This is inferred in the text (page 7, lines 23-25) but is not stated in a clear and direct manner. The authors should more clearly define what is meant (functionally) by SVOC and LVOC.*

Author's answer

1. An additional section, **Section 2.2 Thermal volatility measurements** has been added to clarify the volatility-based assumptions and classifications that have been used in this study.

Referee's comment

*2. Page 4, line 10: Do the authors mean "If the aerosol chemical composition is strongly size-dependent...."?*

Author's answer

2. This section (**Section 2.3**) has been significantly rewritten, and this comment has been incorporated into the new discussion.

Referee's comment

*3. The authors should ensure all references are accurate. For example, Cerully et al. (2017) and Huldebrandt Ruiz et al. (2015) were both published in Atmos. Chem. Phys. but their references indicate Atmos. Meas. Tech. as journal in which they were published.*

Author's answer

3. Thank you for identifying these errors. All references have been checked and corrected.