

Response to Reviewer #RC2

General comment

Organic aerosols are a major contributor to total aerosol mass concentrations and have implications for both human health and climate change. However, the formation of organic aerosols involves a variety of chemical and physical processes in the atmosphere, resulting in complex particle compositions. Therefore, the measurement and quantification of particle composition, especially at the molecular level, has been a long-standing measurement technology challenge that is critical for a better understanding of the sources and formation mechanisms of organic aerosols.

This paper presents an improved thermal desorption technique, the Vaporization Inlet for Aerosols (VIA), coupled to the NO₃-CIMS. The VIA inlet removes gas compounds with an activated carbon denuder, vaporizes particles in a heated tube, and transfers the thermally desorbed vapors to the NO₃-CIMS with a newly designed sheath flow interface. The authors demonstrate that the VIA inlet can efficiently remove background gas compounds while maintaining high transmission of particles larger than 50 nm, and that the sheath flow interface achieves low detection limits of desorbed vapors due to reduced wall loss. In addition, the authors show that the VIA inlet can also be operated in a temperature ramping mode, where the volatility of particulate compounds can be probed through thermogram analysis. The scientific topic of this paper is important, the measurement technique is novel, and the technique characterization is comprehensive. Overall, this is a relevant study that fits within the scope of the AMT. However, some technical details need further clarification and discussion to make it more useful to the community. Here are my main questions/comments:

We thank the reviewer for the positive and insightful comments, and we answer the specific comments point-by-point below. The reviewer's comments are in **blue**, and our answers are in **black**.

Specific comments

Comment #1:

While the VIA-NO₃-CIMS is an online technique when operating at a fixed T, it appears to have long duty cycles (hours) for T ramping. Are there limitations that prevent rapid ramping? If so, the authors should mention them in the main text, as volatility measurement is a key feature of this technique.

Response:

The main factor that limits the time resolution in the current setup is the time needed for cooling after a heating ramp. As noted in Section 3.4, at least 20-30 minutes are needed for its natural cooling down to room temperature. We also discuss the potential for active cooling in this section, which could increase the time resolution if implemented.

If the hardware does not introduce limitations to the time resolution, the next limitation comes when we start ramping rapidly enough that the shapes of the thermograms become noisy due to shorter data averaging at each temperature. At this point, the feasible maximum ramping rate becomes a function of the aerosol loading. Nevertheless, we expect that around one hour for a full cycle (up and down ramp) is feasible, and if data from both ramps can be used, this provides an effective time resolution of 30 minutes. We modified the discussions in line 508 to clearly point out the two factors that prevent rapid temperature ramping, i.e. the lack of a cooling system and enough data points to fit the thermograms with more accurately.

Comment #2:

When operating in T-ramping mode, whether particles are fully evaporated can be judged from the shape of the thermograms. However, when operating at a fixed T for high time resolution, it's less obvious to me how to tell if 0.1 s residence time is sufficient for complete evaporation, especially for aerosol loading in polluted environments. And this introduces quantification uncertainties into the online measurement. The authors should discuss this.

Response:

This is a very good point. For the application in field or laboratory settings where fast changes in aerosol loadings are expected, e.g. close to primary sources, it may be more useful measure at one fixed temperature (which can evaporate the most fraction of SOA particles). This does add uncertainty to the quantification but will provide better chemical information of rapidly changing aerosol components. A compromise could also be to periodically run one temperature scan to get the correction factors, e.g. twice a day. In all cases, having an AMS or SMPS system after the VIA during those scans at the same time would be very helpful to check if the particles evaporated completely and to constrain the fitting. Alternatively, to correct for fast changes in the aerosol loadings, and AMS/SMPS measuring ambient air can be used to normalize the VIA thermograms.

We added the following discussions in Section "3.4 Current challenges and future improvements" covering the limitations of application for field campaigns.

"The application of the VIA-NO₃-CIMS system in the field will be one critical next step. In most cases, using the ramping mode is to be preferred, as the additional information from the thermograms aid both quantification and estimations of volatility. Fixing the thermal desorption temperature could be preferable under conditions where aerosol loadings are expected to change on short time scales, e.g. close to large primary emissions. In these cases, quantification is limited, but chemical information can be obtained from short-term plumes. As a compromise, most of the time measuring at one fixed temperature (which can evaporate the major fraction of OA), but running entire temperature scans routinely to get the correction factors, e.g. twice a day, could be an option. In addition, having an AMS or SMPS system after the VIA during scans at the same time would be very helpful to check if the particles evaporated completely. Though there would also be value in having an AMS/SMPS measuring ambient air all the time to provide information on how the total OA signal changes throughout a ramp. At some point it is clear that the sensitivity of the VIA system becomes the limiting factor in capturing very fast changes in the composition."

Comment #3:

Thermogram analysis and the corresponding 1-D model are valid for a constant particle source. However, if the T ramp takes hours (or even 10s of mins), how would this technique account for variations in particle composition and size distribution for ambient measurements?

Response:

It is clear that in conditions where large changes in the aerosol types and loadings take place on the time scale of 10s of minutes, the VIA is not going to be optimal. We refer to our response to Comment #2 where we also addressed this issue.

Comment #4:

The authors attribute the decreasing HOM signals after reaching their maximums to the vapor wall loss in the vaporization tube. It's true that molecular diffusion, and thus wall loss, increases with temperature, but I'm not entirely convinced that this can cause > 90% loss as shown in Fig S14. Could this decrease also be thermal decomposition? The lack of double modes in the thermograms may simply be that the

decomposition products are less oxygenated, which escapes detection by NO₃-CIMS. The authors would need to justify their conclusion.

Response:

The reviewer is correct that thermal decomposition is likely to play an important role, and the loss to the VIA walls was indeed assumed to be leading to decomposition and not solely being condensational loss. In fact, condensation is less likely as the VIA walls are hotter than the air in the VIA during the measurements, and if the molecules evaporate in the middle of the VIA, they should not stick to the warmer walls. The observed thermograms of sulfuric acid supported this hypothesis. In addition, we observed near-unit transmission of 13 tested VOCs within the thermal desorption tubing (Fig. S4 & S5).

Instead, as the reviewer speculated, there are chemical processes (possibly thermal decomposition) responsible for the vapor loss of these labile HOM molecules after they hit the hot wall. The main effect, leading to the steep decline in the thermograms is not mainly from diffusion increasing with temperature (although this also takes place), but the species evaporating earlier in the tube, thus having more time to diffuse to the walls.

We mentioned in the Abstract and the Conclusion that “*the loss potentially leads to fragmentation products that are not observable by the NO₃-CIMS.*” To make this issue more clear, we also made modifications to indicate that the loss is likely chemical loss instead of the physical condensational wall loss in line 398, “*...higher temperatures might cause earlier evaporation within the vaporization tube, thus leading to larger losses (i.e. HOM vapors collide with the walls and decompose).*” and in line 465, “*We suspect this loss is mainly owing to that HOM molecules were lost upon impacting the walls of the vaporization tube, then decomposing to fragmentation products that are not detectable by the NO₃-CIMS.*”

Future work will aim to combine the VIA inlet with other detectors to also investigate the fates of less oxygenated compounds (and hopefully the thermal decomposition products as well) in SOA particles.

Comment #5:

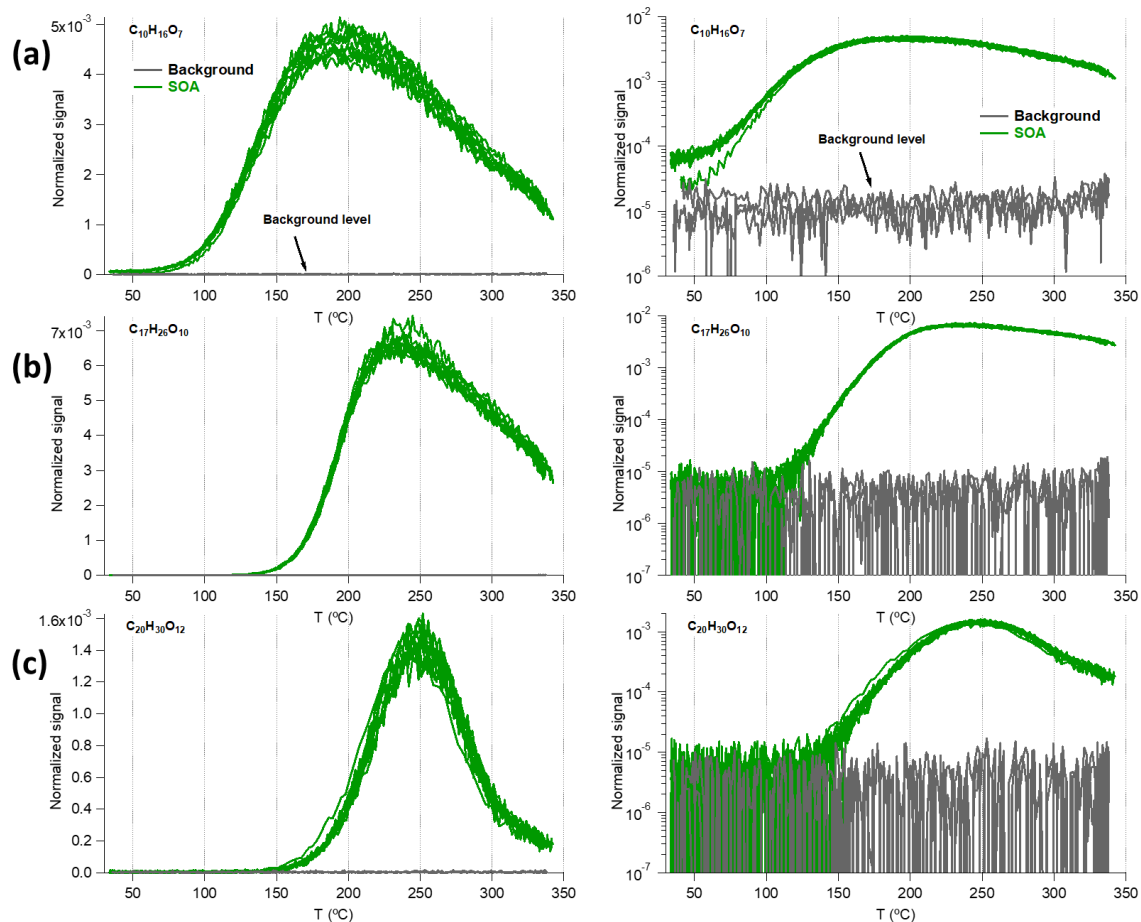
If the vapor wall loss in the vaporization tube is indeed significant, this can introduce contaminations due to the wall memory effect when the VIA is cooled and heated again (e.g., Fig S10b). What level of quantification uncertainty would be introduced in the continuous operation of the T-ramping mode?

Response:

The comparable results from continuous steps down and ramping up runs in Figure S10 qualitatively indicates that the memory effects using the VIA-NO₃-CIMS is negligible. In order to quantify the memory effects of potential contaminations, we did one experiment in a 2 m³ Teflon chamber. We included 3 background measurements: before, during, and after 12 continuous ramping scans (90 ppb of α -pinene and 62 ppb O₃).

In general, the relative contributions of contamination to the measured total signals are less than 2%, even smaller than the precision of the 12 scans (i.e., standard deviation, 4.6%). Thus, we attached both the 12 SOA measurement and 3 background scans of some HOM peaks in the supplementary (as Figure S14) to show the negligible background levels compared to the measurements. The following description was added in line 437 “*Reproducible thermograms were obtained using a steady SOA input and showed negligible background levels during continuous ramping mode (Fig. S14).*”

Overall, the contaminations and corresponding memory effects should not be a concern while using this setup (at least with SOA mass concentrations less than 40 $\mu\text{g m}^{-3}$ based on our tests).



“Figure S14. Thermograms during SOA (green lines) and background (gray lines) measurements. The left panels are in linear scale, while the right panels are in log scale. The experiment was conducted in a 2 m³ Teflon chamber with 90 ppb of α -pinene and 62 ppb O₃. The three background measurements were conducted before, during, and after the 12 continuous ramping scans.”

Comment #6:

Fig 5b & c, why does the HOM trace in stepping mode seem less stable and smooth than in ramping mode?

Response:

At lower temperatures (30-150 °C), both modes are relatively stable. However, when the temperature increases further up, the steps-mode measurements are not that flat anymore. In fact, the ramping-mode measurements start to show larger variations compared to lower temperatures as well, but less significant than the steps mode.

We suspect that this fluctuation might be related to the temperature-induced changes in the flows in the CIMS inlet. As shown in Fig. R1, the sum of reagent ions showed an opposite trend to the variations of the VIA temperature. As a result, normalizing the measured HOM signals to the total reagent ions could largely compensate for this fluctuation. This is partly why we did not include a part to explicitly discuss this fluctuation of reagent ions in the first place and we try to make the discussion relatively easy to follow and less redundant. Since normalization is usually the first step to do during the data analysis, we should have done the normalization for Fig. 5b & c as we did in other figures (e.g. Fig. 5a). Thus, we modified this figure in the manuscript accordingly and attached the revised version below. Now, the measurements of both modes are more comparable than before.

On the other hand, the temperature-dependent variation of the reagent ions (and total ion counts) during ramping mode are smoother than these step changes (blue curve in Figure R1). We found out that the mass loading of particles might also relate to this variation, but we do not have a clear explanation so far. Thus, we added some discussions on this issue in Section 3.4 “Current challenges and future improvements” to inform this variation of reagent ions during temperature changes to the reviewer and readers.

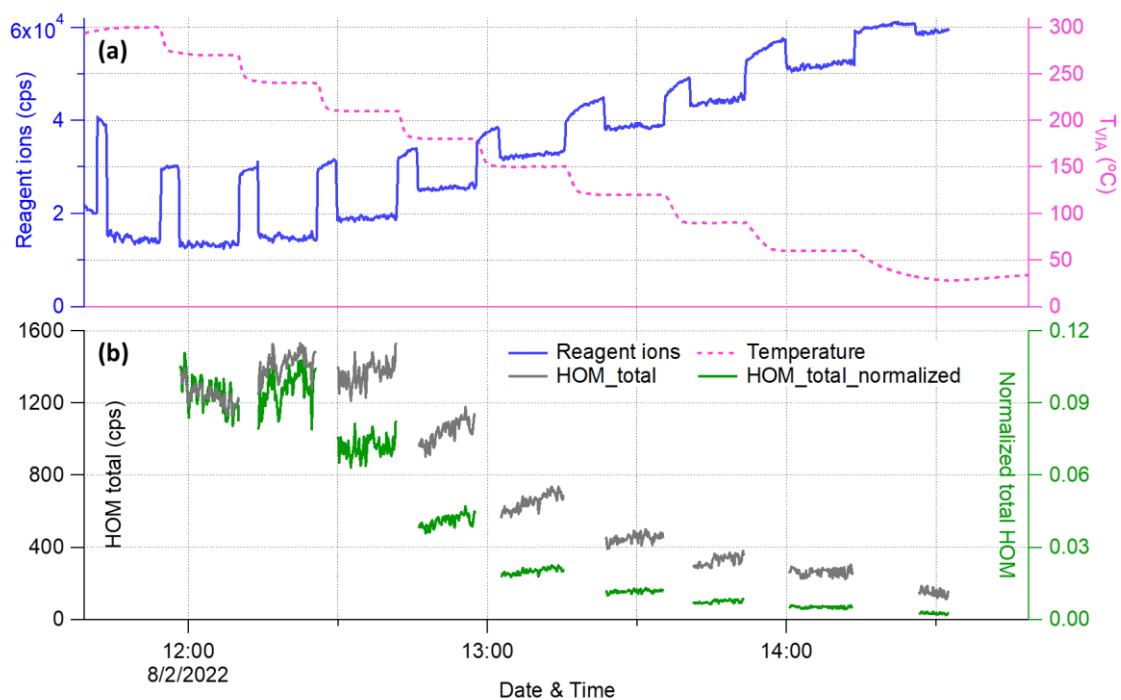
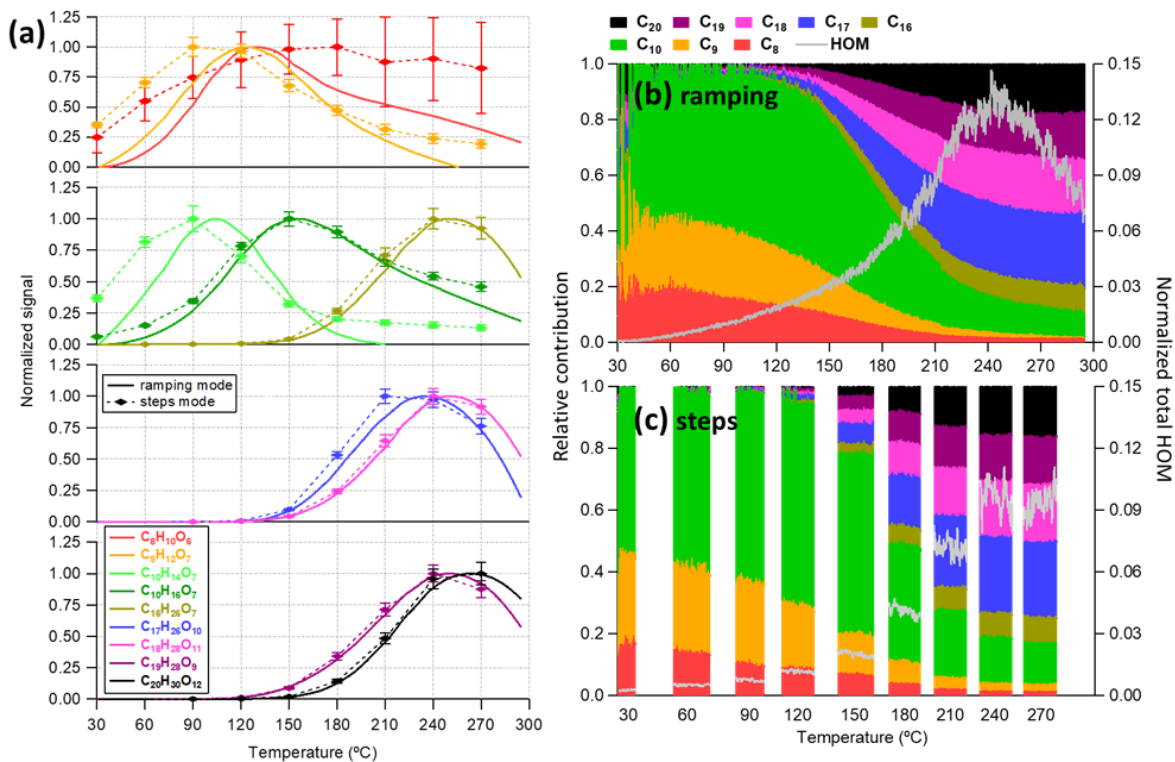


Figure R1. Time series of (a) reagent ions (i.e. sum of nitrate ion monomer, dimer, and trimer signals) and the VIA temperature, (b) raw (gray lines) and normalized (green lines) total HOM signals.



“Figure 5. Comparison of measurements obtained between the ramping and the steps mode for (a) thermogram of some chosen HOM monomers and dimers, and (b, c) the relative contributions of different C number families to the total HOM signals. In (a), smoothed signals are shown for the ramping mode (“Loess” algorithm with a bandwidth of 0.25 and the second order local polynomial was used), while the mean (diamond markers) and standard deviation (bottom and top whiskers) are shown for the steps mode. The thermograms are normalized to the reagent ions first and then to their maximums. The raw signals of the same dataset are given in Fig. S10.”

Reference:

Lopez-Hilfiker, F. D., Mohr, C., Ehn, M., Rubach, F., Kleist, E., Wildt, J., Mentel, T. F., Lutz, A., Hallquist, M., Worsnop, D., and Thornton, J. A.: A novel method for online analysis of gas and particle composition: description and evaluation of a Filter Inlet for Gases and AEROsols (FIGAERO), *Atmos. Meas. Tech.*, 7, 983-1001, 10.5194/amt-7-983-2014, 2014.