The authors thank the reviewer for the careful review of our manuscript and the helpful comments and suggestions. All the comments (in black) are addressed point by point, with our response in blue, and the corresponding revisions to the manuscript in red.

Review # 3

Gao et al. presented a novel technique WALL-E, which is a thermal desorption unit coupled with CIMS. It can detect and quantify the chemical composition of aerosol particles with CIMS in real-time. This study is very interesting and innovative. However, the manuscript's readability could be improved. I recommend a major revision prior to publication. Please see my detailed comments below:

General comments:

1. Stainless steel tubing was used for WALL-E in this study. Uncoated stainless steel tubing can adsorb semi-volatile and polar organics at elevated temperature, leading to sample loss and memory effects. Did you use any inert-coating on these tubes? if not, I recommend using inert-coated tubing (e.g. sulfinert coated stainless steel tubing) in the future, and add discussion of the caveat of using uncoated stainless steel tubing

The system was not coated during the experiments presented in this study, but coating will be implemented in future developments to further reduce potential wall interactions

Lines 171-174: *"A limitation of the current design is the use of uncoated stainless steel, which can lead to adsorption or memory effects for more-volatile compounds. Inert coatings will be considered in future iterations to further minimize wall interactions."*

2. SMPS was used in the experiments, and I wonder if the evaporation efficiency, T_{50}, and volatility characterization are particle size and mass loading dependent? Please include the number and size distribution for standards and SOA. Are SMPS and CIMS measure the same particles?

This has been previously discussed in Zhao et al. (2024), who showed that the evaporation within the TD is not size-dependent at temperatures greater than 300 °C. All experiments performed in this work (besides the temperature ramp) were performed at 320 °C, so we do not expect any size dependencies in the results presented here.

Chemical characterization of α-pinene-derived SOA, the SMPS, and the WALL-E system were positioned at the same distance, using the same tubing material and having the same sampling flow. As a result, both instruments measured the same particles.

3. There are two figure S5 and two figure S6 in the SI. It's very hard to follow which plot is being referred to. Please correct.

They are now corrected.

4. For the sensitivity calibration, the unit of ncps/(ug/m^3) was used. When comparing the sensitivity among different compounds and calibration (second figure S6 and figure S8), the unit of ncps/ppm should be used to eliminate the influence of molecular weight.

Because this is a particle phase measurement, the unit ug/m^3 is determined based on the averaged expected particle density (i.e., reported density for a pure product) and not a gas phase concentration. As a result, the use of ncps/ppm is not appropriate in this case.

5. In section 3.3.2, the usage of T_{max} and T_{50} is confusing. The T_{max} in FIGAERO usually refer to the temperature at which the signal intensity is maximum. For VIA, people usually use T_{50} as well instead of T_{max}, as VIA thermogram also shows a sigmoid curve instead of a near-Gaussian shape. The WALL-E and VIA both have continuous aerosol flow into the TD, therefore they have similar thermograms. The T_{max} for FIGAERO and T_{50} for VIA and WALL-E both represent the temperature when the desorption rate is maximum.

We agree that T_{50} is more appropriate for WALL-E due to its sigmoidal thermograms, and it is the main metric used for volatility analysis in this work. T_{max} is included only for comparison with other systems where it has traditionally been used. While T_{50} was used in one VIA study to describe volatility trends across PMF factors (Li et al., 2023), most VIA studies, including the PEG-based calibration, use T_{max} to derive volatility (C*) (Zhao et al., 2024). Regarding thermogram shapes, thermal decomposition can result in steep decreases after T_{max}, which is not observed with WALL-E, where a near-sigmoid profile is obtained

6. Are all the standards and SOA particles fully evaporated after passing through the WALL-E?

The mass remaining in the particles after the evaporation in WALL-E is dependent on the sample flow and particle mass (Figure R2). Therefore, according to the flow used in this work for SOA experiments, we expect that > 94% particles were evaporated.

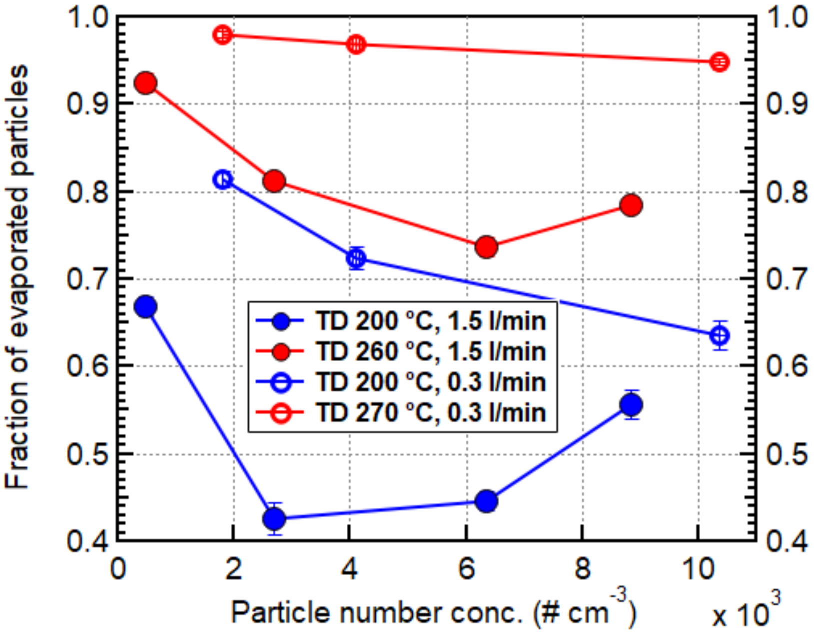


Figure R2. The fraction of evaporated particles corresponding to the particle number concentration under different sample flows (0.3-1.5 SLPM).

For the standards, reported in Figure S8, the sensitivity of shikimic acid and glucose are outlier compounds which the sensitivities are lower than expected (the fitted sigmoidal curve). This may indicate the partial evaporation of those low-volatile species or an error in the averaged density.

We added a sentence.

Line 402-406: *"Among all calibrated compounds, two outliers exist (i.e., shikimic acid and glucose), which might be due to partial evaporation leading to an underestimation of the sensitivity. When excluding these two species, the estimate of total particle mass concentration is closer (with 36% overestimation) to the total particle mass concentration measured by the SMPS as depicted in Figure 5."*

Specific comments:

1. Line 38: T_{50} is not defined in the abstract.

It's now added.

Lines 40 – 41: *"In addition, the measured T_{50} (the temperature at which 50% of a compound evaporates), for…"*

2. Line 157: what is the residence time in the TD with sample flow rate at 1 SLPM?

The residence time at 1 SLPM flow is between 70-90 ms, depending on the hot flow (0 - 0.5 SLPM).

Lines 178 – 180: *"At a sample flow rate of 1 SLPM, the residence time in the TD is estimated to be between 70 and 90 ms, depending on the added hot dilution flow (0 to 0.5 SLPM)."*

3. Line 217: what are the densities used for the mass concentration calculated by SMPS for each compounds? Consider include into table S2.

The density for each compound was added to Table S1.

4. Line 233: how is OH radical generated in the OFR? Please include the ozone concentration, relative humidity, and OH exposure in the table S3, as O_3/OH initiated oxidation was mentioned.

OH radicals are generated in the reaction of VOC + O_3. As we did not add any OH scavenger, the yield of OH radicals is expected to be ~85%, which has been reported by other studies (Rickard et al., 1999; Paulson, 1998). Unfortunately, the O_3 concentration was not measured. We added relative humidity in Table S3.

5. Line 294: any results indicating the better flow stability with the presence of a HF?

As shown in Figures 3C and D, the addition of the HF improves the evaporation and the transfer of the compounds to the dilution unit.

6. Line 317-318: I wonder if you observe any trimers? How about the sulfur containing compounds shown in figure 5B, as SO_2 was added into the system.

No, we did not detect trimer signals as their masses might be outside the measurement range of the CIMS used (i.e., up to m/Q 700). The mass fraction of S-containing compounds is <5%.

7. Line 326: what is ncps? Normalized count per seconds? How are they normalized?

We added the definition and clarify the normalization.

Line 280: *"All product ions are normalized to the Br⁻ signals."*

Line 347 - 348: *"It has an unexpected high background of ~0.04 normalized counts per second (ncps) when there is no VOC injected."*

8. Line 330-331: "without sensitivity correction, …, mass is 1.0 ± 0.1 μg/m^3" 0.04 ncps is the same as the background as mentioned in line 326. I'm not sure if I fully understand this sentence here.

The mass spectra presented in this work (including Figure 4 and lines 330-331) are background-subtracted. The total signal of all detected SOA compounds is ~0.08 ncps (without background subtraction) and ~0.04 ncps (after background subtraction) when the particle mass is 1.0 ± 0.1 μg m-3. However, the high background of 0.04 ncps in line 326 refers to the individual compound $C_8H_{12}O_4$, which could be a contamination compound from the flow tube. Therefore, the SOA signal must not be the background noise.

9. Line 356: Figure S8, why shikimic acid and glucose were excluded? Any criteria?

As shown in Figure S8, shikimic acid and glucose were outliers from the fitted sigmoidal curve. As discussed in previous studies, selected standard compounds might induce uncertainty in the sensitivity estimations (Zaytsev et al., 2019; Bi et al., 2021; Song et al., 2024). Therefore, to get a better calibration curve, we presented and discussed the results obtained with and without the outliners to evaluate the uncertainties associated with the approach.

One potential explanation for the lower sensitivity of shikimic acid and glucose is the partial evaporation of the compounds. We have added a sentence regarding the potential reason.

Line 402-406: *"Among all calibrated compounds, two outliers exist (i.e., shikimic acid and glucose), which are most likely due to partial evaporation leading to an underestimation of the sensitivity. When excluding these two species, the estimate of total particle mass concentration is closer (with 36% overestimation) to the total particle mass concentration measured by the SMPS as depicted in Figure 5."*

10. Line 388-390: how is sulfuric acid formed in the OFR? The particle phase H_2SO_4 mass loading seems to be pretty high. Any further discussion regarding the H_2SO_4? "a good agreement is retrieved" I'm not sure if I fully understand this. Were you saying the SMPS results match the CIMS results? But how can SPMS differentiate organic and inorganic? The mass loading reported with 10 compounds fitting (8.7 μg/m^3) is higher than that with 8 compounds fitting (6.4 μg/m^3), but the 10-compounds lead to underestimation, and 8 compounds lead to overestimation. Please correct.

Since SO_2 was added to promote the particle formation and to generate more SOA mass (Stangl et al., 2019), sulfuric acid (H_2SO_4) was formed via the reaction between SO_2 and OH (and O_3 and Criegee radicals), which is a very well-known chemical process leading to sulfuric acid.

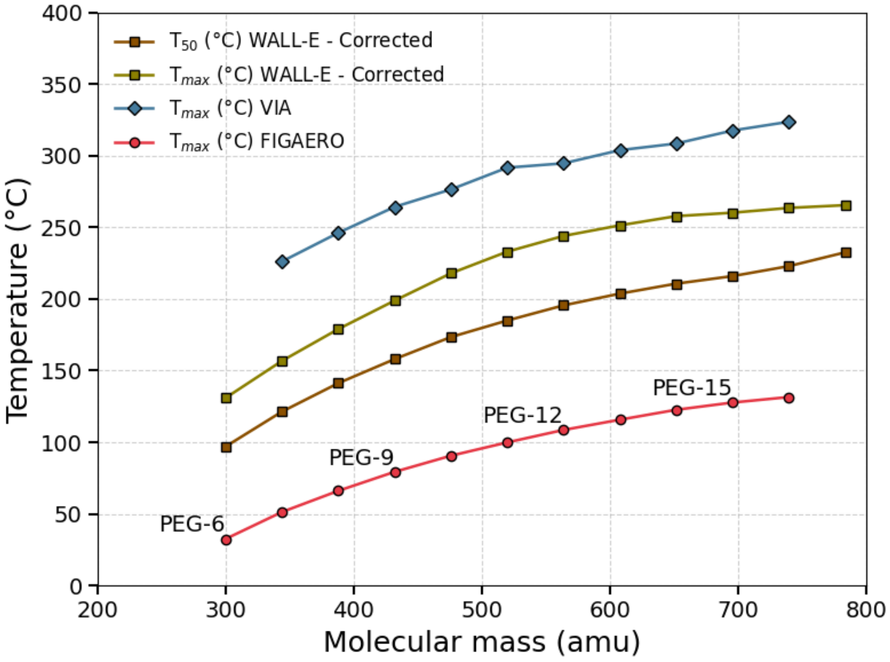
The concentrations of sulfuric acid obtained from the direct calibration (i.e., Figure S2) and the declustering method were compared, providing an opportunity to evaluate the declustering method.

We correct the 'underestimation' and 'overestimation' in the sentence as follows:

Lines 414 - 417: *"A good agreement between the direct calibration (Table S2) and the declustering scan method is retrieved (7% overestimation and 25% underestimation for the 10 and 8-compounds fit, respectively underlining the benefit of using this approach to obtain the concentrations of organic and inorganic present in the particles."*

11. Line 454-455: as mentioned in the general comment 4, I'm not sure if you should use T_{max} from WALL-E to compare with other particle evaporators, or use T_{50}, which is the temperature when the desorption rate is maximum.

In this case, using either T_{max} or T_{50} would not make a significant difference for what we are trying to demonstrate, as both values have similar slopes and fall between the VIA and FIGAERO results. T_{max} is used for comparison with prior studies. The following plot includes the added T_{50} values for reference.



T_{50} will be adopted as the primary metric for volatility characterization in future WALL-E studies.

12. Line 461-463: any explanation for the signal decrease after they reach the plateau? Also why this is an improvement compared to other online TD techniques?

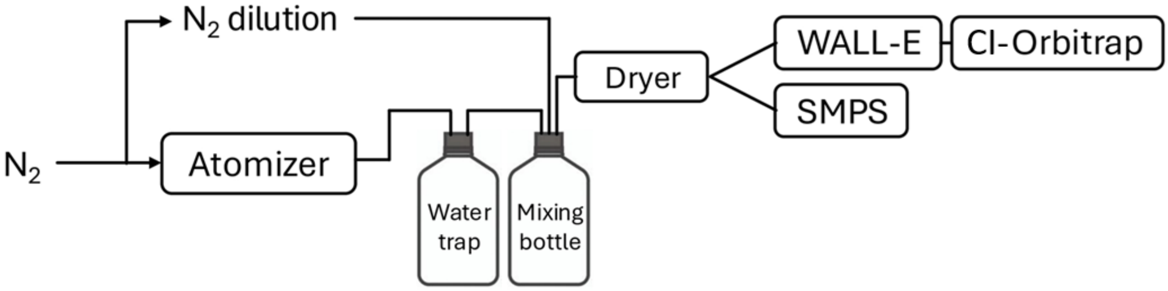
We attribute the signal decrease after reaching the plateau to thermal decomposition or additional losses occurring beyond T_{max}. In other systems, this decrease is typically much steeper and does not follow a sigmoidal behavior; instead, the signal often drops rapidly, resembling a Gaussian shape. The improvement in our system is the ability to maintain a near-sigmoidal thermogram, indicating smoother evaporation and net reduction of the fragmentation compared to other online TD techniques.

13. Line 479-487: when you mention the T_{max} for VIA, do you mean the gas temperature or measured temperature? As far as I know, VIA does not measure the gas temperature directly.

The T_{max} reported in previous VIA studies represents the set value of the TD part, not the direct measurement of the gas.

14. Figure S1: chemical ionization section is not mentioned in the plot.

The plot was modified, and CI was added to the instrument box



15. Figure S4: for the lower plot, what does the time in x-axis mean? What different conditions are they corresponding to?

The time on the x-axis corresponds to the continuous temperature ramping process, not to averaged values at each set temperature. This plot shows how closely the signal remained around zero throughout the entire heating and cooling cycle from 0 °C to 390 °C and back to 0 °C.

16. Figure S12: please specify the legend. Also from the main text, I understand the reason to include the comparison between 99.5% and 98%. But why include 40% and 60%? T_{50} should be from your sigmoid fitting results as mentioned in the main text.

The 40% and 60% thresholds were included to demonstrate that even if the fit is not ideal—which is not the goal but can occur in practice—the resulting error in volatility estimation remains negligible. The 10% variation was intentionally exaggerated to illustrate the limited impact of such deviations.

17. Figure S15: do you mean T_{max} or T_{50}? T_{50} in the plot, but T_{max} in the caption and main text.

It’s corrected now.