We thank both reviewers for their comments. We have included the reviewers' comments below in black text and our responses are in blue text. Additions to the manuscript are in *italics*.

RC1:

This manuscript develops a new technique called VIA-CI-IMS-TOF for online and isomer-resolved aerosol chemical analysis. The authors evaluated the performance of this instrumentation using 10 different carboxylic acids over a wide range of temperature. They further applied this technique into a chamber experiment with ozonolysis of a-pinene, which is able to prove its ability for identifying some isomers at real time. SOA are complicated mixture with diverse composition and structures. IMS is a promising technique coupling with MS for real-time isomer-resolved measurement. This technique is expected to deepen our molecular-level characterization and understanding of SOA. I strongly recommend its publication after addressing the below comments

We thank the reviewer for their reading of the manuscript, recommendation of publication, and specific comments on how we can improve the text. Please see our responses below.

Major comments

1. I never work with VIA and CI-IMS-TOF. Coupling both is a smart idea and the key aspect of this study. Since VIA and CI-IMS-TOF are both commercially available, I wonder whether this combination (or so-called coupling) could be readily used/achieved straightforward if both are available? What is the key challenge of achieving such combination?

Yes, the VIA and the CI-IMS-TOF are both commercially available from Aerodyne and Tofwerk. Coupling the VIA with the CI-IMS-TOF is very straightforward, only requiring a single wired connection and common hardware to connect the VIA to the AIM inlet. Both the VIA and the CI-IMS-TOF can be controlled by a single computer and the signals from each are logged in a single data file. The key challenges to this coupling are twofold: 1) installing the VIA in a manner that minimizes the transmission of unevaporated particles to the AIM inlet (in this case, a 90° connection was used with a vacuum line to remove particles from the sample flow) and 2) minimizing the effects of changing sample temperature on IMS pressure and performance (achieved here using drift time calibration).

2. I also wonder whether it is possible to achieve real-time and isomer-resolved gas-phase and particle-phase analysis simultaneously during one single chamber experiment, e.g. by switching two lines of charcoal denuder and HEPA particle filter in front of VIA?

This is an excellent idea that could be explored in future applications of the VIA-CI-IMS-TOF. Gas- and particle-phase switching was initially considered for this study but was determined to be out of the scope of this work. A key consideration for this approach is that analyte losses, delay times, and filter/denuder efficiencies would need to be characterized. Additionally, it would have to be decided whether to flow the filtered (particle-free) air through the heated VIA or not, as doing so may result in undesired thermal decomposition of some gas-phase analytes. The use of a denuder and HEPA filter upstream of an aerosol inlet was described by Eichler et al. (2015) in their publication on the chemical analysis of aerosol online (CHARON) inlet. A similar approach could feasibly be taken for use with the VIA-CI-IMS-TOF. To incorporate this idea into the publication, we have added the following to lines 388-390 in the revised manuscript:

"Additionally, near-simultaneous analysis of gas- and particle-phase analytes could be achieved by alternating the sampling flow between a denuder and a particle filter installed upstream of the VIA."

3. Line 145-150 The authors mentioned that standards are vaporized into the chamber and then condensing onto seed particle, as their first sets of chamber expts. What type of seed particles is used during these expts? Is there any specific reason that standards are prepared in methanol not water?

No seed particles were used for these experiments as the dicarboxylic acid standards have sufficiently low volatility to nucleate upon injection into the chamber. To clarify this, the following text was added to line 148 in the revised manuscript:

"…without the use of seed particles."

The carboxylic acid standards are poorly soluble in water at room temperature (especially those C_8 and larger), so methanol was used to avoid solubility issues. For example, the mole fraction solubility of suberic acid ($C_8H_{14}O_4$) in water at 24 °C is ~2.00×10^{-4} (~1.93 mg mL^{-1}), which is ~160 times lower than its solubility in methanol (Yu et al., 2012). As the carbon chain length is increased, this solubility drops further; the water solubility of azelaic acid ($C_9H_{14}O_4$) at 25 °C is ~1.78 mg mL^{-1} (Apelblat and Manzurola, 1990).

Also, I am a bit confused with the later text that some standards were pipetted onto a PTFE filter that placed between VIA and AIM (CI-IMS-TOF), but using heated chamber air to evaporate analytes from PTFE filter. It seems these are two methods of bringing standards into the instrument. Why two methods are required? Are they targeting for different standards? Can the authors explain why not directly injecting these standards by nebulizing the standard solution into organic particles following a dryer before entering into VIA-CI-IMS-TOF?

Two methods for analyzing standards were required here due to having very limited quantities (~1-2 mg) of the α-pinene ozonolysis product standards. While it would have been preferable to use the same method for both sets of standards, we did not have enough of these standards to achieve sufficient concentrations in the environmental chamber. The PTFE filter method provided good CI-IMS-TOF signal while only using a small quantity of each α-pinene ozonolysis product standard. While the proposed approach would work and may more accurately mimic the behavior of real aerosols, it would require a more complex experimental setup than we used. As we were only intending to measure the IMS drift time and not to quantitatively determine sensitivity, we decided to use the simplest method possible.

4. Fig. 1 shows that these standards are nicely separated at different drift time. Can drift time information be used to infer to some chemical properties? e.g. HPLC retention time is an indicator of polarity. Also, why only using carboxylic acids as standards in the entire study? Could this

technique apply for other non-carboxylic acid compounds such as esters, peroxides, carbonyls, etc?

Drift time is related to the collision cross section of an analyte cluster. Thus, calculated collision cross sections can be used to estimate drift times if the ion drift region is sufficiently characterized. We recommend viewing Rutherford (2026; Ph.D. thesis chapter provided to reviewers prior to publication), who describe in detail the relationship between drift time and analyte structure in this CI-IMS-TOF.

Carboxylic acids were used because a) they are very readily detected using both I^- and Br^- and b) their commercial availability and low volatility make them convenient surrogates for SOA constituents. Additionally, we have previously used most of these standards to evaluate a different I-CIMS technique (Schaum et al., 2025) and can thus compare the performance of the two methods for these carboxylic acids. Other non-carboxylic acid compounds could certainly be used, providing that they are commercially available (or can be synthesized), sufficiently stable at the high temperatures in the VIA, and can form adducts with the reagent ion being used. We have added the following text to lines 374-375 in the revised manuscript:

"Provided that other reaction product standards with different functionalities (e.g., peroxides, nitrates) are available (or can be synthesized) and thermally stable, other more complex aerosol systems can also be explored."

5. For this VIA-CI-IMS-TOF technique, I wonder whether it is possible to demonstrate its quantification ability by varying the concentration of standards, and providing quantification capability information such as detection limit (e.g. LOD, LOQ) and linear range like traditional chemical analysis?

It should be possible to calibrate the VIA-CI-IMS-TOF with the method shown in Schaum et al. (2025), which used liquid chromatography and a VIA coupled with an I-CIMS, or with a liquid calibration system such as the Calibration Apparatus for Manual Injection of Liquid Standards (CAMILS) developed by Davern et al. (2024). However, one would need to carefully characterize losses of analytes to tubing, the VIA, and the AIM inlet to accurately determine sensitivity if these methods were used. A method for introducing standards that uses a nebulizer and dryer, as mentioned above in comment 3, could also be used providing that the nebulization efficiency and analyte loss are well characterized.

6. For chamber expt as shown in Fig. 3 and Fig. 5, many isomer peaks are not baseline separated. Is there any hope that this issue could be further improved in IMS settings?

It is possible that baseline separation can be achieved for some analyte mixtures by modifying the IMS settings, though this was not a priority for this study. For example, adjusting the travelling wave frequency and voltage can have large effects on separation that are dependent on the collision cross sections of the ions of interest (Rutherford, 2026). A user can tune the travelling wave parameters to achieve the best possible separation for the compounds that are being studied.

7. I also wonder how did the authors fit those not-well-resolved peaks, e.g. how the software treating the data automatically and identifying those isomer peaks in IMS for each m/z? Currently only a few formulas with standards are shown for chamber SOA, but I assume there should be many isomer peaks for many other compounds. I wonder how many isomers are found for other formulas, e.g. dimers and other compounds? The most simple way is to show a typical molecular fingerprint like HPLC-HRMS using rt vs. m/z, therefore I am curious if the authors could provide a scatter plot and/or excel sheet for chamber a-pinene SOA, by showing drift time vs. m/z while dots were coloured by peak area/intensity? This plot could be used in the maintext to strengthen the current method for a broader identification of isomer-resolved peaks

While Tofware uses multi-peak fitting to extract time series of overlapping isobars in the mass spectrum, this cannot be used for extracting drift time profiles. For that, the software uses a simple m/z range centered on the exact mass of the target analyte. It is possible that drift time peaks may result from mass peaks close to a target peak (*i.e.*, some peaks in an IMS spectrum may be from a different m/z than the target), so the m/z range can be narrowed to get a more isolated drift time profile at the expense of signal intensity.

For this study, we focused only on the molecular formulas for which we had authentic standards. Many other compounds with multiple isomers were detected and we have shown those in a new two-dimensional image plot showing ion signal versus drift time and m/z. We have added this new figure to the Supplemental:

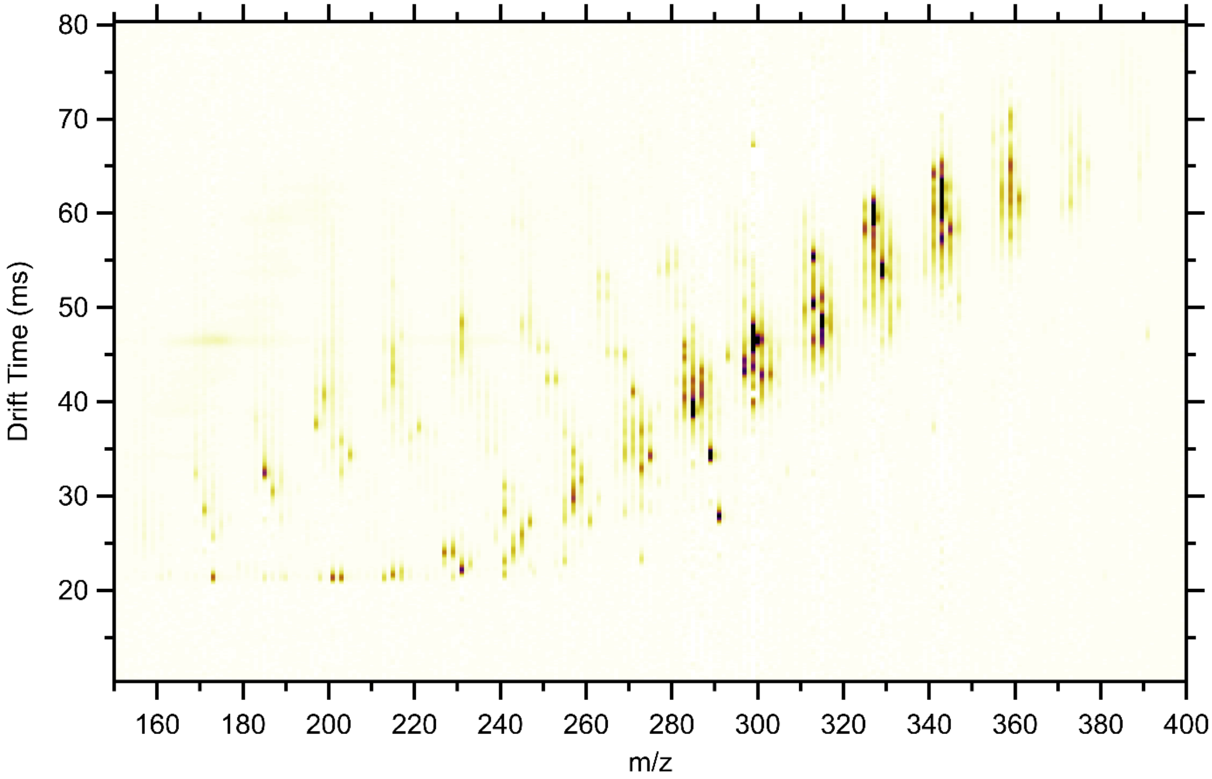


Figure S7. A 2-dimensional image plot of I^- adduct drift time versus m/z (I^- mass included) averaged over the second half of the chamber experiment (~40 min). Signal strength is depicted by the color gradient with stronger signals appearing the darkest.

The following text has also been added to lines 210-211 in the revised manuscript:

"Numerous compounds were detected in the SOA by the VIA-CI-IMS-TOF (Fig. S7), but only the molecular formulas for which we had standards are discussed here."

8. It seems there are two identical chamber SOA expts but switching between Br- and I- reagent, am I right? For Fig. 5, I guess Br- and I- give two different drift tube time for each standard. Can the authors label the name of the corresponding isomer peak for each standard? Indeed, Br- and I- reagent ions could provide more detailed chemical information, but it might also make the data analysis and interpretation even more complicated, and I think the current result is still very preliminary.

Correct, these data are from two different chamber experiments that were measured separately with I^- and Br^- reagent ions. The two reagent ions give different drift times because they have different collision cross sections when clustered with the same analyte.

We have labeled the standards in Fig. 5 and fixed an error in the data processing that had resulted in an inflated number of IMS peaks for $C_9H_{14}O_4$ in bromide mode. The main text has been updated to reflect this change. The updated figure and caption are below.

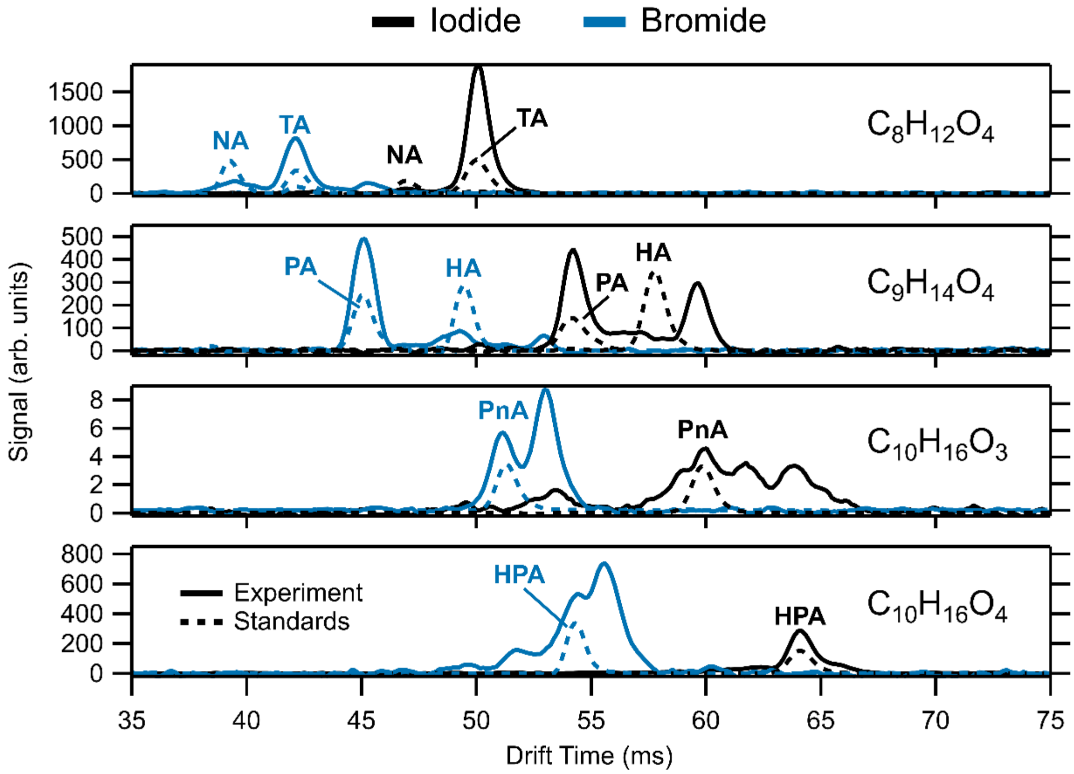


Figure 5: Ion mobility spectra of four chemical formulas clustered with I⁻ or Br⁻ ions observed during the α-pinene oxidation experiments. Data from the chamber experiments are displayed as solid lines and the synthetic standards are shown as dashed lines. The standards are labelled as the following: NA = norpinic acid, TA = terpenylic acid, PA = pinic acid, HA = homoterpenylic acid, PnA = pinonic acid, HPA = 10-hydroxypinonic acid.

While it is true that data analysis becomes more complicated with the addition of more reagent ions, the user can decide whether the additional chemical information is worth the added analytical complexity. This may not be true in all cases, but we show in this study that complimentary information can be gained using the ability of the AIM inlet to rapidly change reagent ions.

9. I could not find the detailed information that how the drift time calibration was performed in sec 3.1. If I understand correctly, this drift time calibration is only necessary for VIA temperature ramping experiment. It seems VIA was operated at a fixed temperature of 200 C for chamber SOA expts. Is there any specific reason of choosing this fixed temperature that is different than ramping 30-170 C used for standards? By the way, would VIA operating at multiple temperature give more information?

We describe the details of the drift time calibration in section 2.3. The drift time calibration was most important for the temperature ramping experiment, but it is likely best to use it for all experiments to account for any drift in performance. The higher temperature of 200 °C was used to help ensure complete evaporation of the SOA in case there were compounds with lower volatility than ant of the standards. Yes, varying the temperature of the VIA could provide information on the volatility of the analytes. By showing that the Tofware IMS software package can correct for temperature-induced drift time changes, future work with the VIA-CI-IMS-TOF could use temperature ramping to investigate volatility differences between reaction product isomers in SOA.

The following text was added to lines 365-366 of the revised manuscript:

"…or operation at multiple fixed temperatures…"

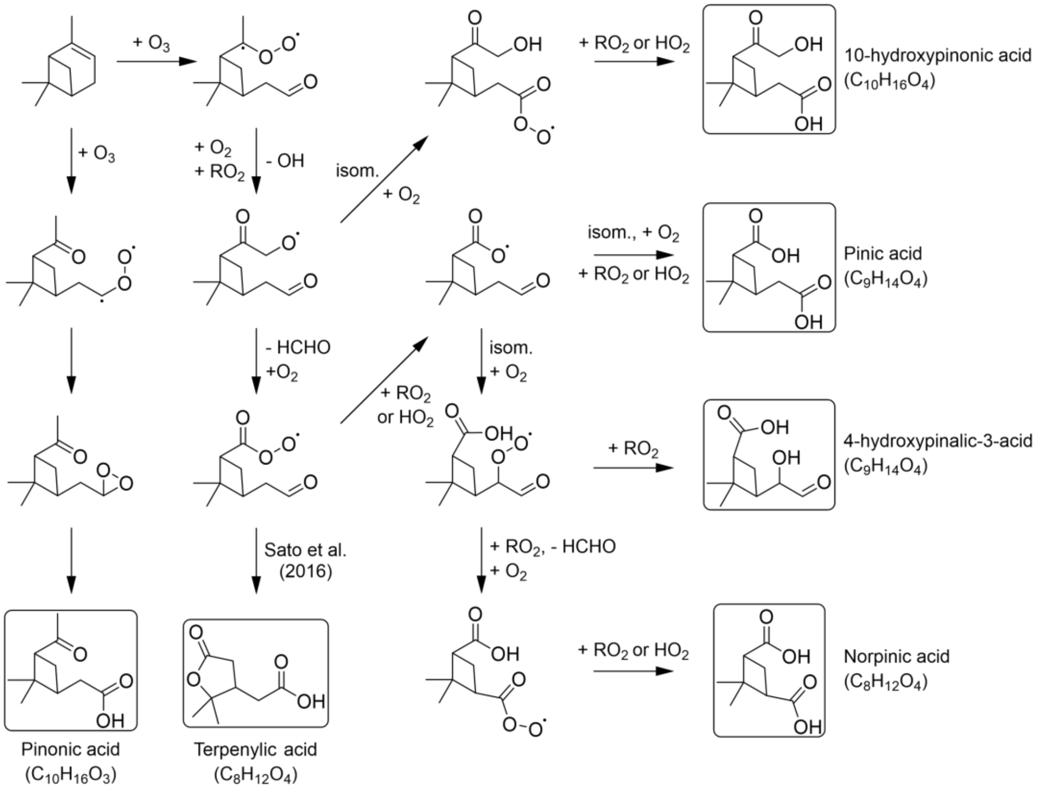
Minor comments

Line133 "peak s" → "peaks"

This error appears to have been introduced during the preprint formatting. We have confirmed that it is not present in the revised manuscript.

For Fig. 2, terpenylic acid formula should be $C_8H_{12}O_4$

This error has been corrected and a new version of Fig. 2 has been added to the revised manuscript.



For the data showing in Fig. 3 and Fig. 5, what is the IMS collected time during the chamber SOA expt? Are they referring to the averaged ~1 minute near the end of the experiment?

Yes, the IMS data shown in Figs. 3 and 5 are averaged over 1 minute near the end of the experiment.

RC2:

The manuscript presents a novel analytical platform for in-situ isomer-resolved characterization of organic aerosol components by coupling a Vaporization Inlet for Aerosols (VIA) with a chemical ionization ion mobility time-of-flight mass spectrometer (CI-IMS-TOF). The approach provides important analytical methodology for separation and chemical characterization of OA-relevant isomers. The study demonstrates that ion mobility separation remains reasonably stable under heated aerosol vaporization conditions and enables direct online identification and temporal tracking of individual OA isomers formed during α-pinene ozonolysis. In selected case study, distinct formation behaviors of structurally similar compounds have been recorded and use of complementary reagent ions (I^- and Br^-) has been demonstrated indicating potential to expand molecular coverage. Together, these advances establish a useful analytical capability for investigating OA composition, reaction mechanisms, and physicochemical evolution with improved structural and temporal resolution. The manuscript is well written, logically organized, and supported by clear figures. Overall, it presents a compelling contribution to the field and is recommended for publication after minor revisions.

We thank the reviewer for their thoughtful comments and suggestions on the manuscript. We appreciate the recommendation for publication and have addressed the comments below.

In addition to the list of conceptual questions already raised by the first reviewer, several additional aspects would benefit from further clarification and elaboration.

- For comparison with previous studies and to establish a reference framework for future IMS applications, the manuscript would benefit from reporting calculated collision cross section (CCS) values for the analyzed species.

Calculating CCS values is a complex task that is out of the scope of this study. We have provided a chapter from a recent Ph.D. thesis (Rutherford, 2026), which uses the CI-IMS-TOF and computational methods to explore the relationship between adduct structure and CCS.

The following text has been added to lines 381-383 in the revised manuscript:

"The use of multiple reagent ions can also play a role in compound identification, as recently shown by Rutherford et al. (2026) who used computational methods and IMS-MS data to predict structures and mobilities of I- and Br- adducts."

- The transferability of the presented approach beyond the well-characterized α-pinene SOA system is neither demonstrated nor sufficiently discussed. It remains unclear how the method would perform when applied to substantially more chemically complex real-world aerosols, such as BBOA or anthropogenic SOA, where greater molecular diversity, matrix effects, and broader volatility distributions may influence separation performance and detection efficiency.

Our primary aim is to demonstrate this technique for use with laboratory-generated SOA, which has been shown in the manuscript. We agree that challenges may arise when applying this technique to more complex aerosols, though these challenges are not unique to the VIA-CI-IMS-TOF. The α-pinene SOA system is frequently used to demonstrate new analytical techniques and is sufficiently complex to extrapolate performance to other SOA systems.

Previous applications of the VIA and IMS have been successfully used to analyze complex aerosols, such as field-collected urban OA (Schaum et al., 2025) and ambient aerosol samples collected during the Southern Oxidant and Aerosol Study (SOAS) campaign (Krechmer et al., 2016), respectively. Although we did not explicitly demonstrate the use of the VIA-CI-IMS-TOF with ambient OA, the ability to separate analytes by mass, mobility, volatility (by changing the VIA temperature), and ion affinity (by using multiple reagent ions) provides many paths toward characterization of complex aerosols and was discussed in the manuscript. To highlight this point, we have added the following text to the revised manuscript based on several reviewer comments:

"Provided that other reaction product standards with different functionalities (e.g., peroxides, nitrates) are available (or can be synthesized) and thermally stable, other more complex aerosol systems can also be explored." (Lines 374-375)

"The use of multiple reagent ions can also play a role in compound identification, as recently shown by Rutherford et al. (2026) who used computational methods and IMS-MS data to predict structures and mobilities of I- and Br- adducts." (Lines 381-383)

"…or operation at multiple fixed temperatures…" (Lines 365-366)

We believe that these additions adequately address the reviewer's concerns about the translatability of this technique to more complex aerosols.

References

Apelblat, A. and Manzurola, E.: Solubility of suberic, azelaic, levulinic, glycolic, and diglycolic acids in water from 278.25 K to 361.35 K, J. Chem Thermodynamics, 22, 289–292, https://doi.org/10.1016/0021-9614(90)90201-Z, 1990.

Eichler, P., Müller, M., D'Anna, B., and Wisthaler, A.: A novel inlet system for online chemical analysis of semi-volatile submicron particulate matter, Atmos. Meas. Tech., 8, 1353–1360, https://doi.org/10.5194/amt-8-1353-2015, 2015.

J. Davern, M., V. West, G., A. Eichler, C. M., J. Turpin, B., Zhang, Y., and D. Surratt, J.: External liquid calibration method for iodide chemical ionization mass spectrometry enables quantification of gas-phase per- and polyfluoroalkyl substances (PFAS) dynamics in indoor air, Analyst, 149, 3405–3415, https://doi.org/10.1039/D4AN00100A, 2024.

Krechmer, J. E., Groessl, M., Zhang, X., Junninen, H., Massoli, P., Lambe, A. T., Kimmel, J. R., Cubison, M. J., Graf, S., Lin, Y. H., Budisulistiorini, S. H., Zhang, H., Surratt, J. D., Knochenmuss, R., Jayne, J. T., Worsnop, D. R., Jimenez, J. L., and Canagaratna, M. R.: Ion mobility spectrometry-mass spectrometry (IMS-MS) for on- and offline analysis of atmospheric gas and aerosol species, Atmos. Meas. Tech., 9, 3245–3262, https://doi.org/10.5194/amt-9-3245-2016, 2016.

Rutherford, M.: Emissions and Chemistry of Volatile Organic Compounds in Indoor and Ambient Environments, Ph.D. Thesis, University of Colorado Boulder, Boulder, Colorado, 202 pp., 2026.

Schaum, A. F., Bates, K. H., Min, K.-E., Myers, F., Longnecker, E. R., Canagaratna, M. R., Alton, M. W., and Ziemann, P. J.: A simple, versatile approach for coupling a liquid chromatograph and chemical ionization mass spectrometer for offline analysis of organic aerosol, Aerosol Res, 3, 557–568, https://doi.org/10.5194/ar-3-557-2025, 2025.

Yu, Q., Ma, X., and Gao, W.: Determination of the solubility, dissolution enthalpy and entropy of suberic acid in different solvents, Fluid Phase Equilibria, 330, 44–47, https://doi.org/10.1016/j.fluid.2012.06.012, 2012.