

Interactive comment on “Clustering, Methodology, and Mechanistic Insights Into Acetate Chemical Ionization Using High-Resolution Time-of-Flight Mass Spectrometry” by Patrick Brophy and Delphine K. Farmer

Anonymous Referee #2

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The manuscript by Brophy and Farmer presents a very innovative and rich set of laboratory experiments to characterize analytical performance of the acetate TOF-CIMS running in the negative ion mode. One challenge is that analyte ions have different fates depending on different mechanisms (e.g. clustering, self-clustering, proton abstraction, fragmentation) and not all necessarily occur in the IMR. This important issue is nicely shown to be complex for quantification and points to the need for better understanding of the instrumental settings and operation modes. The challenges are well characterized in this manuscript. Furthermore, the sensitivities and limits of detection of selected ions are thoroughly examined as a function of different instrumental vari-

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ables (voltages, etc.), which allow for assessing the importance of different components of the CIMS instrument (API, etc.). Ambient conditions (e.g. RH), previously thought to be of relatively low significance, turn out to be critical as the water cluster is shown to compete with other clusters. The bulk analysis of an example complex oxygenated mixture from PAM chamber points to difficulties in accurate mass defect distributions, O/C ratios and carbon numbers. Despite the new knowledge on the challenges, the progress seems promising and it is impressive how very low detection limits for the organic acids can be achieved.

Overall, I find this paper extremely relevant for AMT and it is recommended that it is considered for publication, although I guess it is still possible to make further enhancements to the story and below are just a few suggestions which might further inspire the discussion or clarity.

General:

1) In this relatively complex API instrument design, different settings (and their interplay) can make a huge impact on measured ion distributions and overall analytical performance but they are not always used consistently by the community and a way to standardize or normalize the settings could be proposed. The authors did an excellent job with applying Thuner algorithms to investigate different setting optima and, among others, pointing to how the component voltages can impact the characteristic voltage differences. While the comprehensiveness and detail of the analysis are outstanding, I was somewhat missing the stronger and perhaps a little more optimistic visioning relevant for real atmosphere measurements where mixtures of acids, peroxides, esters and other potentially interfering ions could be present. Could approaches like fast switching of optimal configurations favoring clustering or declustering regimes, variable E/N settings at constant API settings alternating with variable API settings at constant E/N settings, or other be an inspiration for readers?

2) The unselfish sharing of absolute values of various hardware and software settings

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(e.g. Thuner) such as presented here is exemplary and should become the standard for future work. Furthermore, such an excellent use of the Thuner capabilities seems particularly valuable to control clustering while optimizing the ion transmission. I find the Thuner application description very interesting. Perhaps it would be even more relevant to make its own section in the main text instead of the SI.

3) In the calibrations the authors focused on relatively small set of standards (mostly organic acids which behave similarly) and the PAM example of complex mixture is on the other extreme. In addition, the number of ions used in the Thuner is relatively small and in the low mass range. This observation should not be regarded as criticism as I am simply curious why the authors did not try to optimize the detection of specific ions on a more diverse group of chemicals (e.g. diols, esters, peroxides) across a broader mass range? This could potentially be helpful for optimizing to both the sensitive and selective detection of ions of interest while still allow for desensitizing the system to undesired ions.

4) Because the E/N concept cannot explain fully ion-molecule collisional dissociations, one needs to understand what happens with the ions at different stages beyond the IMR chamber. It could still be instructive for readers if the standardized IMR conditions were proposed which could facilitate the comparisons between different instruments.

Specific

5) L.229 "TOF duty cycle corrections are made at m/z 59 for all data collected". It would be useful for some readers to describe explicitly how this was done. Please provide description or reference the approach because there are sometimes inconsistencies in how duty cycle is defined and corrected for.

6) Sect. 2.2 the calibration setup generates single component standards. Did you try making the multicomponent standards as well? For example, could be useful with Thuner optimizations?

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7) L 177 I would not expect that the instrument saw many or abundant heavy ions, but I wonder if you can be convinced that the ions larger than m/z 494 did not wrap around the mass scale to appear at the subsequent cycle (at the wrong mass)? For example, in Fig. 3 the ions look somewhat cut-off but they may have been minor anyway. Also have you identified what these high molecular weight ions are (i.e. between 400 and 500 Th)?

8) Table S3 shows ions that were used with Thuner. Depending on which ions were chosen in the sensitivity column 3 it could lead to different optimization results. Would it not make even more sense to include other desired ions from analytical standards in addition to formate ion, spanning the broader m/z range?

9) Sect. 2.4. Do you know or is it worth discussing how the cleanliness of the skimmers (and perhaps other components) would impact the results (e.g. de-clustering) and if that could be responsible for differences between the newer and older instruments if these components are old and never cleaned?

10) The experiments and calibrations use the concept of relative humidity. Would it not be more relevant to operate in absolute humidity? Was the temperature always the same?

11) The paper contains many useful observations improving understanding of observed ions, for example, [acetate + C₂H₃O₅]⁻ which is indicated as a potential product of autooxidation which can be eliminated by removing O₂ from the reaction chamber. Can oxygen from the ambient sample be an issue for this and similar reactions?

Technical

12) L183 What was the internal diameter of the 1/8" OD tubing?

13) L. 207 what materials was the solenoid valve made of? Any other information (orifice, dead volume)?

14) Figure 7. The differences in vertical are difficult to see clearly. Might consider

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making the figure less stretched-out in horizontal.

15) Fig S1, - Consider adding flow rates, tube diameters and tube materials, on the diagram if not presented in the text. -Was the RH sensor in the line to the instrument (rather than in the vent)? If so, was it not the source of any detectable impurities?

16) Table SI2, Even though it might be obvious, the units should be included (both in the case of voltages and pressures (Primary beam region).

17) SI Line 51, change Figure SI1 to Figure SI2

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