# Characterization of a Portable, Light-Weight, Low-Power Chemical Ionization Time-of-Flight Mass Spectrometer

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## Reviewer Responses:

RC1 (Blue).

AC (Black)

### General Comment

The manuscript 'Characterization of a Portable, Light-Weight, Low-Power Chemical Ionization Time-of-Flight Mass Spectrometer' by Dobrecevich et al. introduces a novel, truly portable TOF-CIMS for atmospheric measurements of trace volatiles that can be operated at highest sensitivities. The only presented downside to much bulkier laboratory based or 'transportable' instruments is the reduced mass resolution of only 1300. Nevertheless, with sufficient analytical caution reasonable results can be generated. The authors try to show this with a couple of real world applications.

Although I am deeply convinced by the benefits of a small, light-weight and portable analyzer, I am not entirely satisfied with the analytical characterization of this instrument. My open questions will be addressed in detail in the Specific Comments section. I highly recommend considering these issues with all necessary care to improve the quality of the manuscript.

In addition, there are a plethora of unnecessary mistakes and inconsistencies throughout the manuscript. Follow common guidelines for naming of specific parameters, dimensions, etc. (e.g. IUPAC guidelines of recommendations of nomenclature). Keep the manuscript consistent and do not mix them (e.g. m/z or m/Q or m/Q (Th)). Many of those issues will be highlighted in the Technical Corrections section. Due to time restrictions I can not give a claim of completeness. I recommend careful proofreading prior resubmission.

### Specific Comments

In the following the Specific Comments section is grouped to major and minor comments. Please note, the major comments are not arranged in order of importance! Minor comments are arranged in order of appearance for easier allocation.

### Major Comments

## Ionization

The presented Portable-TOF-CIMS utilizes a Vocus AIM ion-molecule reactor. Being a rather novel technique that certainly differs to previously described TOF-CIMS techniques, there is a limited number of publications available that deal with a thorough characterization of this reduced pressure chemical ionization technique (e.g. Riva et al., 2024, Aggrawal et al., 2025, Song et al., 2026).

We thank the reviewer for the opportunity to clarify the differences of the Vocus Aim reaction cell to previous flow tube based ion molecule reactors whose origins date back to 1966. As described in Riva et al. the Vocus Aim is typically operated at 50 mBar to strike a balance between sensitivity and linear range for general use across a wide array of applications. As a function of increased reaction pressure, the sensitivity increases predictably at constant mass flow through the reactor through a combination of increased collision frequency (pressure) and longer reaction (transit time). It could also be noted that ionization reaction time exists on a spectrum with one end being PTR (~10 us) at low pressures (1-3 mBar) and the other being atmospheric pressure and 100 ms reaction time (Junninen et al., 2010; Rissanen et al., 2019), this would put the AIM reactor solidly in the middle for both pressure (100 mbar) and reaction time (10 ms). In the compact instrument described in this manuscript – we acknowledge this in section 3:Results and Discussion.

We note that the principle of the Aim reactor (a flow tube IMR) is not a new concept, and that in the literature many such reactors are well studied for many different classes of compounds where typical reaction pressures are in the range of 50-250 mbar depending on the reagent ion used.

At the elevated reaction pressures used here the reaction time is indeed longer as noted by the reviewer. The consequence is that the linear range of the instrument at the collision limited sensitivity reduced from ~100 ppbv to ~20 ppbv in this configuration. In practice, as many of the most abundant compounds in the atmosphere are detected at lower sensitivity, the effective linear range is somewhat larger (20-50 ppbv). We also note that Vocus Aim (or flow tube IMRs in general) are best suited for selective ion chemistries for which the longer reaction time is less problematic than general reagent ions (e.g. O2+, H3O+, etc) which are typically operated in PTR style reactors with very short reaction times (100 us) and elevated collision energy.

The references above are also included in the manuscript to form a larger basis set for readers to understand the long history and body of work describing the characterization and ionization properties of flow tube reactors on which this instrument is based.

Aggrawal et al. (2025) constrain the sensitivity towards an analyte of an AIM IMR as a function of the product ion formation rate and the m/z discrimination, often referred to transmission efficiency (reactor, transfer system and TOF analyzer). The former is defined by the reaction conditions (pressure, temperature, reaction time) as well as reaction rate constants.

However, this does not cover the full picture for a flow-driven CIMS operated at ~100 mbar and reaction times in the range of 10 ms. Here, the reality is much more complex and includes equilibrium reactions, side reactions with alternative reagent ions or clusters of reagent ions. Even potential secondary or multiple generation reactions of initially ionized analytes with analytes of higher ionization energy or cluster affinity are reported. These effects together directly affect sensitivities and induce significant matrix effects.

The reviewer summarizes the two dominant effects on sensitivity in a flow tube ion molecule reactor rate constants and transmission efficiencies. The relative transmission efficiency has two main terms, the mass dependence of the ion optics and the binding energy for compounds ionized by adduct ionization mechanisms as described in detail in Lopez-Hilfiker et. al. 2016 and subsequent publications.

Water vapor in the atmosphere often represents the most abundant and highly variable matrix which can effect any chemical ionization mass spectrometer. Operating chemical ionization schemes even at low absolute pressures can exhibit significant water vapor effects and in some cases equilibrium reactions as the reviewer notes (Jobson and McCoskey, 2010; Krechmer et al., 2018; Lee et al., 2014; Mochalski et al., 2019; Murschell et al., 2017; Tani et al., 2004).

Water vapor as a variable matrix component can modify the reaction conditions in flow tube based approaches either by clustering with the reagent ion in the IMR depending on the absolute pressure and thermal energy conditions which ultimately result in competition reactions between water vapor and analytes. For hydrocarbons (in the case of benzene cation reagent ions) or small monoacids (iodide adduct reagent ions) the increasing presence of water vapor primarily limits the availability of the reagent ions resulting lower sensitivities at higher water vapor pressures. In other cases, water vapor may also play a stabilizing role acting as a third body in the net reaction carrying away excess collision energy as is the case during the formation of ion-molecule adducts (e.g. iodide adduct ionization Cl2, ClNO2, N2O5, HNO3, or benzene cations reaction with ammonia resulting in a benzene-ammonia adduct) (Bertram et al., 2011; Kim et al., 2016; Lee et al., 2014). Therefore, depending on the reaction mechanism water vapor may positively or negatively effect the net ionization efficiency.

To quantify the collision limited sensitivity of the instrument, we intentionally use compounds which have been demonstrated in previous work (Aggarwal et al., 2025; Garmash et al., 2024; Lee et al., 2014; Lopez-Hilfiker et al., 2016; Xu et al., 2022) to react at or near the collision limit to define the maximum sensitivity, referred to in the manuscript as the collision limited sensitivity. This is a useful constraint on the sensitivity towards unknown compounds which when applied, gives a lower limit on concentration, and when used in combination with empirical binding energy determinations can reconstruct accurate concentrations. We measure the collision limit in this manuscript using benzene cations, because hydrocarbon standards are much easier to work with than other collision limited compounds and under dry conditions have been shown to react near the collision limit (Aggarwal et al., 2025). In section 3 in the manuscript, we calibrated a multicomponent standard in benzene cation mode to quantify the overall sensitivity achievable with the compact instrument configuration and benchmark the performance relative to other determinations of the collision limited sensitivity in the literature.

In general, as with any chemical ionization mass spectrometer, in some cases, secondary reactions are possible and discussed in some detail in the literature. We note that this is not related to the specific geometries of the reaction cell or the mass analyzer but rather an ion chemistry implementation consideration which should be evaluated relative to the analytes, selected reagent ion and expected concentration ranges. The Vocus Aim flow tube IMR used in this study was operated in a range consistent with a large body of previous work and we defer ion chemistry nuances to the cited references in the manuscript consistent. This is consistent with the scope of this manuscript focusing on the characterization and implementation of existing ion chemistries and reaction cell on a compact analyzer platform.

We have also added the following sentences to the manuscript for clarity:

**At such high sensitivities the linear range of the instrument is somewhat reduced compared to conventional Aim instruments which operate at 50 mbar. We infer a maximum linear detection range of ~20 *ppbv* under dry conditions and about 20-50 *ppbv* under ambient humidities due to the general reduction of hydrocarbon sensitives at elevated humidity (Aggarwal et al., 2025; Kim et al., 2016; Puttu et al., 2026). We note that care must be taken when deploying general reagent ions at high pressures in highly polluted environments or near heavily emitting point sources.**

The proposed ionization pathway is only applicable for another common CIMS technique: A well operated PTR-MS (2-3 mbar, 100 µs reaction time, an E/N to decluster reagent ions) with a significant abundance of reagent ions and only one single ion-molecule reaction that can lead to the ionization of a product (Lindinger et al., 1997). It is well documented that if only one of these parameters is not in the range stated above, the ionization process gets highly nonlinear, especially for complex mixtures like ambient air.

The ionization pathway used in this manuscript is primarily charge transfer with benzene cations and adduct formation for iodide. Both of these techniques are part of a well established body of literature which discusses the benefits and challenges of these reagent (Aggarwal et al., 2025; Kim et al., 2016; Lee et al., 2014; Lopez-Hilfiker et al., 2016). While its true that there are always exceptions to this general statement, notably deprotonation reactions for iodide anions some adduct formation for benzene cations (Kim et al., 2016; Puttu et al., 2026; Zhang and Zhang, 2021) this is also well described in the following references which are cited in section 3.

The reviewers comparison to the reaction conditions of a PTR raises some important distinctions regarding the two ionization approaches. In a PTR reactor the reviewer is correct that the water cluster distribution governs the sensitivity distribution towards analytes and small deviations in the E/N value do significantly effect the ionization pathways by changing the dominant reagent ion present in the reaction cell from (n=1-3 $H(H_2O)_n^+$). These different reagent ions have very different proton affinities thereby impacting selectivity and sensitivity distributions. Despite the short reaction time (typically ~100 us), there are multiple collisions during transit through the reactor and even in PTR sources deviations from the expected kinetically calculated sensitivity are observed (i.e. humidity dependencies and equilibrium reactions are observed for low proton affinity hydrocarbons in general e.g. formaldehyde and benzene). A well-known consequence of using relatively high declustering and collisional energies to control the reagent ion distribution in a PTR based reaction cell is that there is significant ionization induced fragmentation which complicates the mass spectrum. The degree of fragmentation varies depending on the analytes of interest but poses a major analytical challenge to spectral interpretation in complex environments (Coggon et al., 2024; Puttu et al., 2026; Xu et al., 2022).

To operate a hydronium ion based system under flow tube conditions with a similar sensitivity distribution to a conventional PTR would require very low operation pressures and sample flows to have controlled ionization conditions. At such low pressures, collision frequency is reduced and therefore sensitivity can quickly become limiting for most atmospheric measurements.

Flow tube ionization approaches require more selective ion chemistries in general because they are generally operated at higher pressure (to promote sensitivity) and without electric fields to suppress collisionally induced fragmentation. By using more selective ion chemistries (e.g. iodide, bromide, ammonium, benzene cations, amines) the benefits of operating at higher ionization pressures can be realized as the reagent ions are blind to many of the most abundant species which could result in rapid depletion of the reagent ions. The selectivity of the reagent ion must be carefully chosen to match the analytical need such that the analytes of interest are detected but abundant interfering species are not. In the examples of commonly used reagent ions listed above, the selectivity is what allows them to operate at pressures and reaction times much higher than that of a PTR instrument as described by the reviewer, while maintaining linear responses to analytes. The dependencies of the reagent ion distribution flow tube reactors does not critically depend on the E/N (as the electric field is 0) but rather on the distribution of internal ion energy during the reaction. As demonstrated in (Sneha's paper) thermal energy and water vapor are two effects which crucially determine the reagent ion distribution, while the collision energy during transit to the detector impacts primarily the survival efficiency of the weakest ion molecule adducts.

Both ionization strategies (flow tube based CIMS and PTR) have been well characterized as having analyte detection with linear responses within their respective linear ranges (i.e. while there is not significant reduction in reagent ion availability or detector saturation). The reviewer is correct that for some of the concentrations shown in figure 2a we exceed the linear range of benzene cations we have corrected this figure by reducing the range of concentrations demonstrated. Note that while the individual VOC concentrations go up to 3 ppbv this is part of a multi component mixture where the total number of VOC which react with benzene cations is 7 resulting in a total VOC concentration consuming reagent ions of 20 ppbv at 2.5 ppbv individual concentration values.

We have revised Figure 2a and added the following to section 3: Results and Discussion:

This is consistent with the reduction of linear range from ~100 ppbv at 50 mbar given the change in collision frequency and reaction time when operating at 100 mbar as in these experiments. As with any flow tube reactor – a balance between reaction time and reaction pressure must be chosen based on the selectivity of the reagent ion and linear range which is required. While this linear working range would not be appropriate for direct emissions of car exhaust, or near source emissions studies, it is a reasonable working range for the remote atmosphere where the most abundant target analytes may be only 50-100 pptv. To increase the linear range for other applications, dilution, operation at reduced ionization pressure or other measures can be implemented, or a PTR style ionization approach could be used on the same mass spectrometer interface (Claflin, in prep).

All this is directly visible in Figure 2! Just a simple question: At ~ 180 - 200 s (Figure 2) the response to the concentration step of all VOCs is virtually the same with ~30k ncps. Now let's compare xylene and TMB, which both are having very similar m/z, polarities and dipole moments and, hence, very similar collisional rates in a buffer gas. When you claim that sensitivity is collisionally limited, how is it possible that the sensitivity changes from about 1:1 at ~ 180 - 200 s to 3:2 at ~100 - 130 s for the calibration point with ~300k ncps? Also, if xylene is reacting at collisional rate, why is a-pinene showing much higher signals at higher concentrations?

The reviewer is correct that when outside of the linear range, charge competition starts to become a significant effect – this is not necessarily to do with the reaction time but rather the depletion of reagent ions in general. Similar effects can also be observed in a titrated PTR based IMR which becomes organized by proton affinity.

Experimentally we can measure the reagent ion titration effect with an experiment as shown below where constant calibration gas from a bottle is fed into the instrument inlet – a large concentration of a solvent (in the case of benzene reagent ions) is introduced and causes reagent ion titration. We use the deviation in the reagent ion normalized sensitivity to give a guide as to what reagent ion depletion is acceptable to maintain linear response (constant normalized sensitivity).

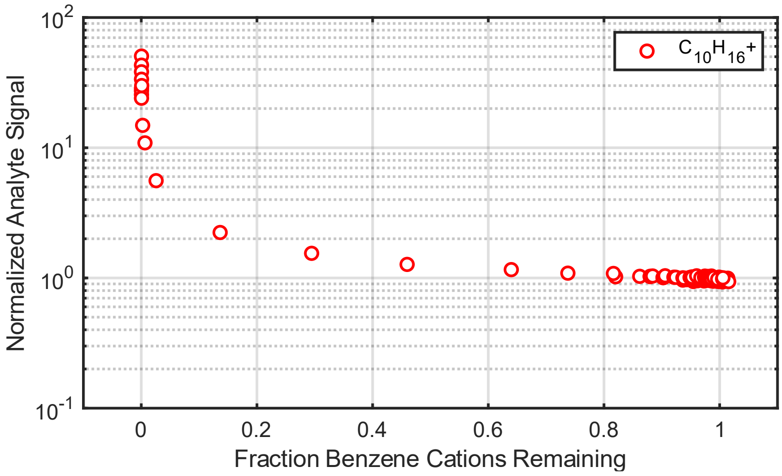
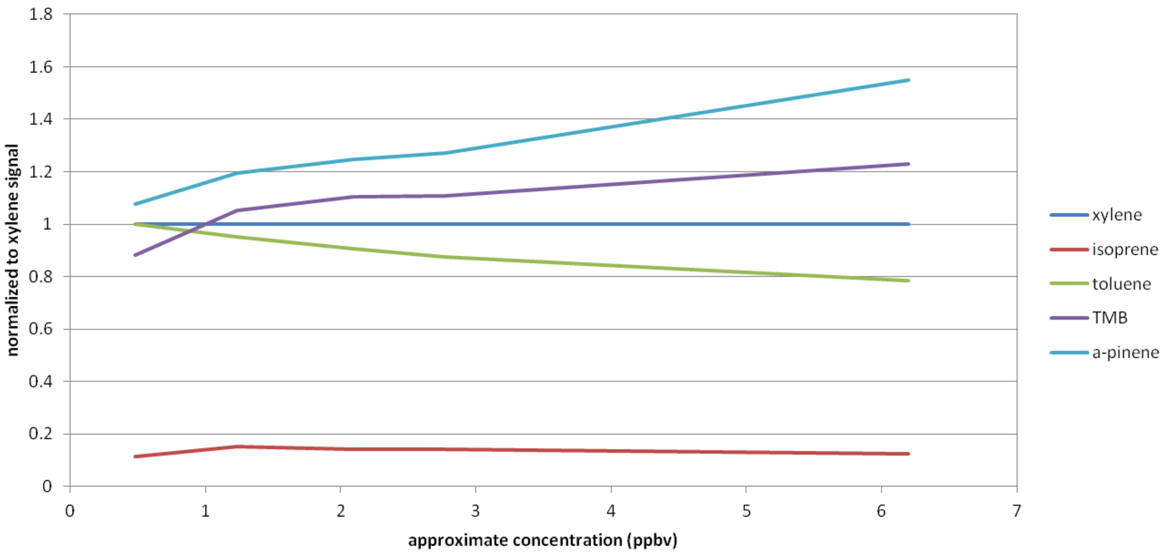


**Figure S3. Relationship between resulting analyte signal and fraction of reagent ion remaining for the detection of α-pinene using a [Bz]+ ionization strategy.**

We thank the reviewer for catching this oversight (too high calibrant gas concentration at the last steps of the calibration sequence) and have corrected this in the manuscript. We have also included the above example figure to the SI and reference it in the text regarding linear range and reagent ion titration in the Results and Discussion Section.

To further illustrate my concerns, I roughly digitized all signals in Figure 2/A and normalized it to the xylene signal intensity:



This figure clearly shows that the whole ionization process is highly nonlinear and actually far away from being collisionally limited.

We have addressed the reviewers comments here in the above sections and responses.

These effects actually do not come to a surprise and are well known and studied for CIMS operated at pressures and reaction times higher than that of a PTR-MS and, hence, I leave it to the authors digging through the abundant relevant literature on this topic.

As this manuscript is titled ‘Characterisation of a Portable, Light-Weight, Low-Power Chemical Ionization Time-of-Flight Mass Spectrometer’ and is introducing a novel atmospheric trace gas monitor, it's clearly the scope of this manuscript to address the ionization process properly.

To save the manuscript, consider the following suggestions:

- refrain from the use of (near) collision limited or standard sensitivity. Yes, a single compound could potentially be ionized at collisional limit (at least in B+ mode, I- is reportedly a three body ionization process) and, yes, it could make sense comparing those to assess instrumental parameters (as shown by Aggrawal et al., 2025).

We have reframed and clarified our use of the collision limited rate as the maximum sensitivity, not that all compounds are collision limited. The collision limit is useful metric to understand the performance of different instruments without having to map between different specified compounds under different reaction conditions; that is - collision limited sensitives provide a universally comparable number for sensitivity between similarly configured instruments. Ultimately, any collision limited rate must adhere to the linear range of the reactor, and conditions which do not for other reasons result in deviations to the ionization rate. This is described in the manuscript at lines 184-195 and in the above reviewer responses.

- Add all 6 VOCs to Figure 2/b, cover the entire range (the calibration was done up to 300k ncps whereas only data up to 100k ncps is shown).

Calibration can only be done in the linear range of the instrument and therefore the measurements made at 300k as noted by the reviewer are not indicative of instrument performance. We have reduced the limits of concentration used and demonstrate linear response in the range which adheres to reasonable reagent ion consumption following Fig. S3 above. For completeness we have put the full dataset and the reagent ion consumption in a supplemental section and it is referenced in the text as how deviations in linearity are observed outside the linear range of the instrument, shown in Fig. S2 below.

- Add the same figure in cps to the supplement and show how the reagent ion is decaying. This can give valuable feedback on linearity when the mixture is not that uniform like in the calibration gas standard.

See the updated figure below:

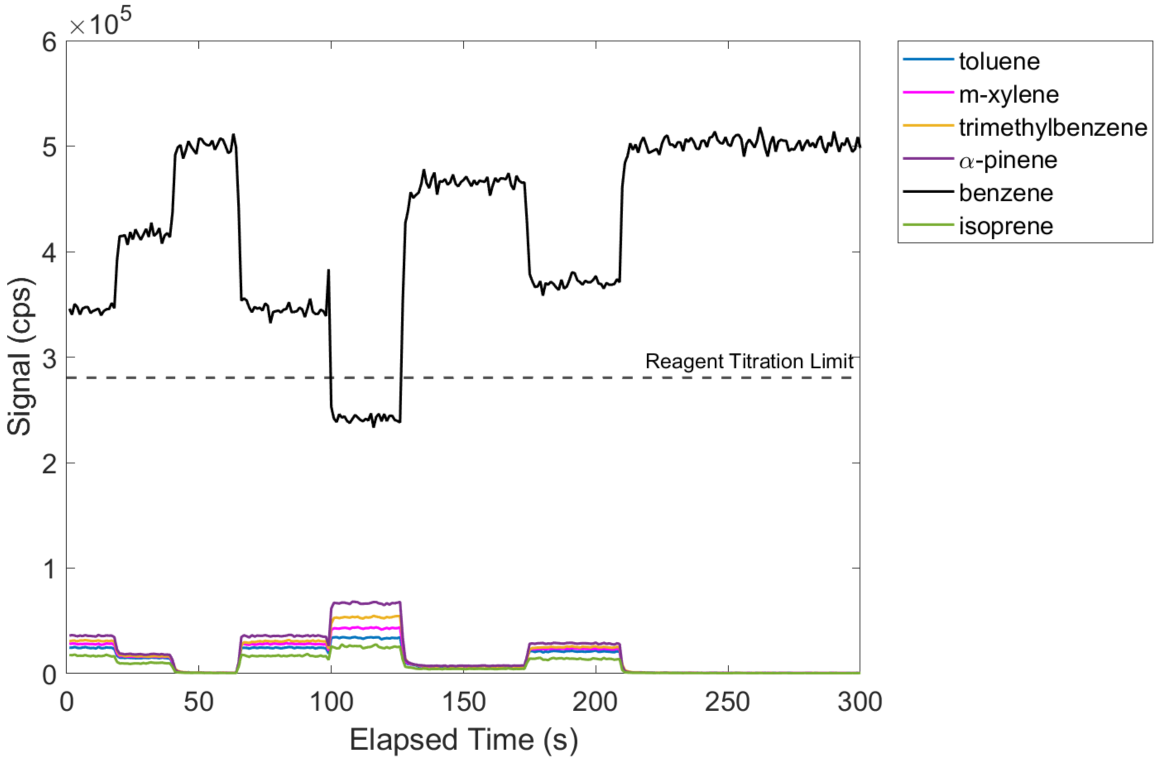


**Figure S2: (a) Raw signals recorded during the calibration for the instrument, tracing the $[Bz]^+$ reagent ion signal pre-normalization. (b) Annotated signals to track the abundance of the reagent ion signal while different concentrations of analytes were introduced into the inlet of the AIM reactor.**

- Add a discussion on the implications for ambient measurements (matrix effects, linearity, etc.).

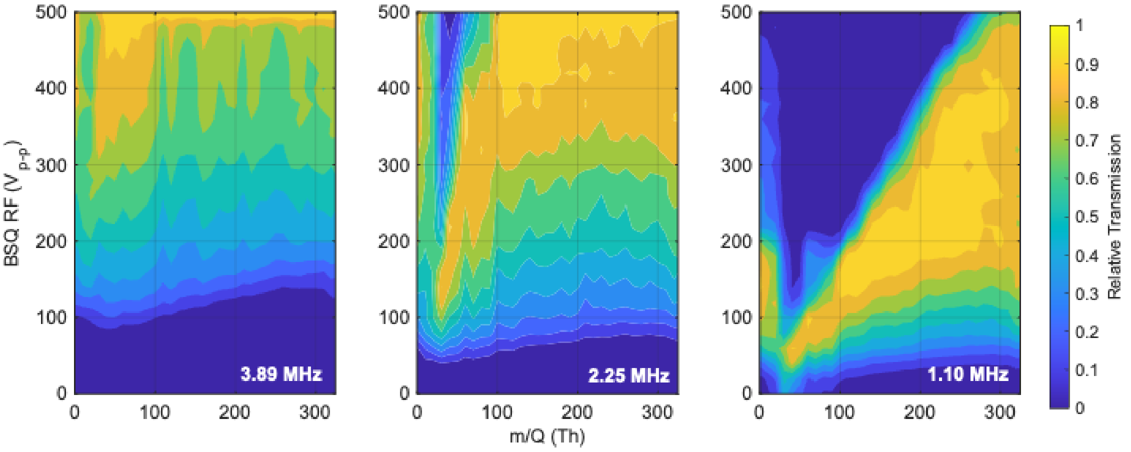
We have added to the manuscript: In polluted ambient sampling environments (e.g., target analyte mixing ratios > 20-50 ppb) a decreased reactor pressure (~50 mbar or larger flow through the IMR) should be considered in order to avoid reagent ion titration, particularly in urban environments with benzene cations. The compact pumping scheme of the instrument provides some constraints on this – entirely limited by the fore pump capacity relative to the incoming gas flows.

### Transmission/Mass Discrimination

The manuscript introduces the use of smaller orifices, other flows and two RF only ion guides and states '*... ion transmission is not affected by the changes in pumping.*' (**L158**). However, with all changes no change in ion transmission would be highly surprising. This is something that needs to be experimentally proven especially when stated directly like this. This is moreover the case, when a constant transmission with the (above discussed) 'collision limited standard sensitivity' is used to calculate quantitative limits of detections covering a m/z range up to *m/z* 1100 (Figure 4).
A solution could be to only compare the xylene sensitivity for both instruments and show the 3 -sigma LODs in units of cps or ncps (for uncalibrated compounds). Make a second plot (or add a second y-axis) where you add the LODs for the quantified compounds of your calibration mix.

The dominant terms affecting the transmission efficiency is the RF amplitude and frequency (at a given pressure). These terms are the same as all Vocus instruments. Despite the differences in orifice sizes, the pressures attained in each of the quadrupole regions are the same. With reduced orifice diameters, the strength of the expansion ('jet') on the downstream side of the pinhole is reduced, and therefore the transport term (residence time) in the first quadrupole is somewhat longer than a system with higher flow rates. This is not entirely problematic, as a weak DC field can be used to compensate and propel ions out of the first quadrupole. The ions in this region are still mostly transported by gas flow (fluid dynamics) rather than electrical potentials.

We have included a figure in the supplemental information with two units, the fundamental ions per second and concentration (xylene equivalent) for the LOD and explicitly state that we assume a constant transmission between the reagent ion and the analyte ions extending to high mass. Such an assumption is supported by simulations of ion trajectories in multipole RF fields as used in the instrument, particularly in the second "BSQ" quadrupole where the mass transmission efficiency matters the most. This is consistent with relative experimental data presented in the supplemental information of Aggarwal et al. (2025).



### Minor Comments

**L81:** Herein the VOCUS AIM is operated at 100 mbar. Riva et al. (2024) introduces standard operation conditions at 50 mbar. Consider discussing the effects of this elevated pressure.

We have addressed these effects in previous reviewer comments above.

**L105:** According to this statement, the accurate quantification directly follows from a limited amount of fragmentation. Of course, this is not true (see Major Comments), but conservation of one chemical composition after ionization undoubtedly simplifies quantification. However, clusters further complicate qualitative and quantitative analyses (similarly to fragments). Clustered products are mentioned and shown throughout the manuscript.

We agree that limited fragmentation indeed simplifies quantification, and also that excessive clustering poses challenges in where to quantify individual compounds. Separating the two steps of ionization and ion transfer can help best understand how to find the optimum parameters. Ionization induced fragmentation is minimized at elevated reaction pressures and thermal reactions, that is without the elevated collision energy which is imparted by the presence of electric fields. Under these conditions additional clustering (for example with water vapor) could present a challenge in determining at what mass to charge one would expect to detect a given analyte. Using the ion optics which transfer the reagent ions and analytes to the mass analyzer at low pressure the transfer collision energies can be adjusted to control the measured cluster distribution by imparting a post ionization collision energy. In general these collision energies are very low, much weaker than the intramolecular bonds and can be selected based on a voltage scanning procedure as described in (Lopez-Hilfiker et al 2016, and subsequent publications) such that spurious water vapor is removed from the analyte ions during transit to the mass analyzer.

**L112:** Polarity switching within 1-2 minutes is actually something new. To my knowledge other bipolar VOCUS AIM instruments have 10 min switching times. I recommend removing this from the experimental section and adding it to the results section together with a figure in the supplement that demonstrates this impressively quick polarity switching.

Reagent ion switching is demonstrated now in the SI with a dedicated figure. Reagent ion switching is limited by the high voltage applied in the TOF and stray charges which may be present on the electrical insulators in the mass analyzer which can cause discharges if not well managed. In this version of the instrument such switching has been demonstrated under real world field conditions to reproducibly reach switching timescales of 1 minute. We note, that care must be taken to maintain a clean dust free system – as dust can cause the charge dissipation to be slow and result in static discharges which could damage the instrument.

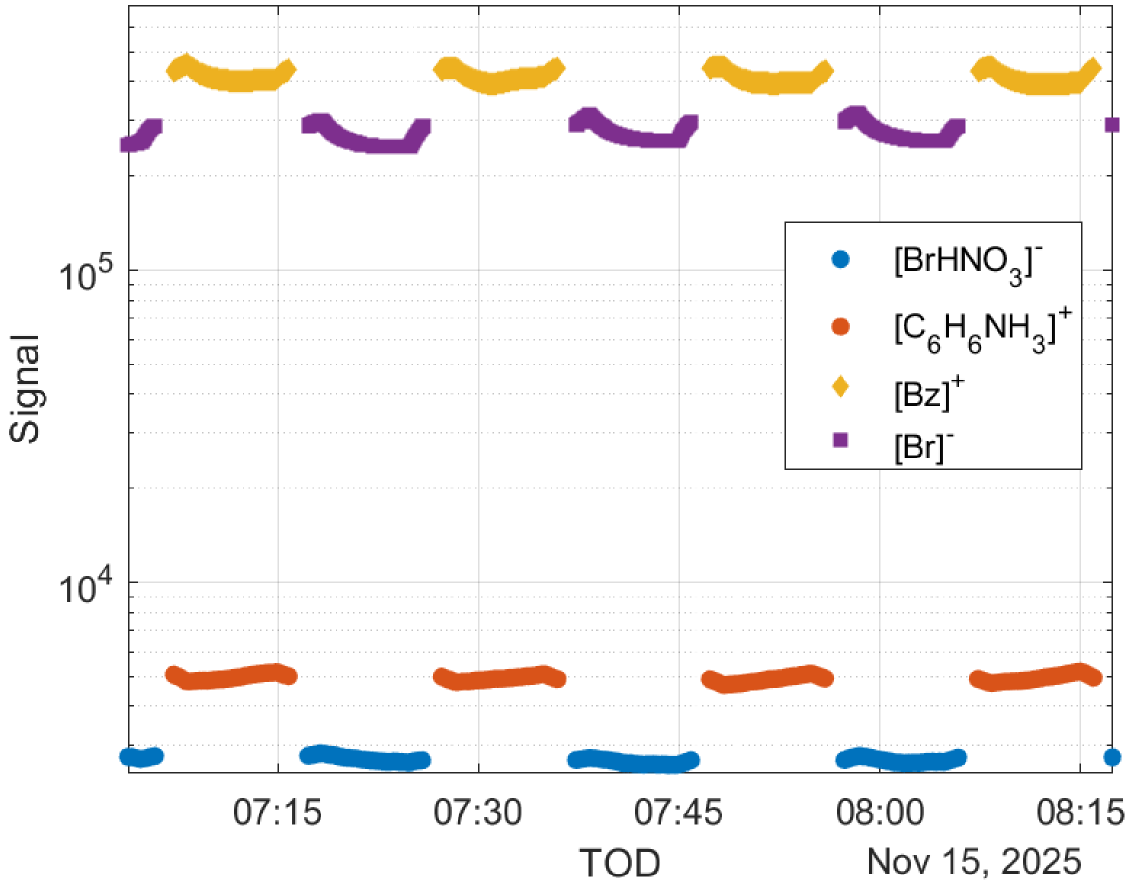


**Figure S1: Time-series showing reagent ion switching every 15 minutes from $[Br]^-$ to $[Bz]^+$ and the normalized analyte signals resulting from the different ionization strategies.**

**L132:** How often was this zero delivered? What periods of time are recommended in between those zeros?

We have updated the manuscript to describe in detail the zeroing procedure of the instrument. In general the zero measurement and duration depends on the timescale of changes which must be captured and the volatility of the analytes. We refer to (Liu et al., 2019; Palm et al., 2019)(Palm et al, also there is an IMR delay paper) for a thorough discussion of instrument zeroing particularly for semi-volatile compounds.

**L148:** Why is primarily the sampling rate of 1 ns limiting the mass accuracy? Based on figure 3/C, the peaks seem to be well characterized and additional data points should not improve the peak-centers dramatically.

The sampling rate determines how frequently the data is recorded and therefore determine the ability of the data acquisition system to capture the true maximum of the mass spectral peak. You can only measure the smallest difference between the true peak maximum and the recorded peak maximum based on the gradation of the recording system ie 1 ns (which corresponds to a mass accuracy of 10 ppm).

**L191:** '*...the detection limit becomes counting statistics dominated (chemical background is negligible).*' I do not understand this. The LOD should always be counting statistics dominated as the chemical background is part of it. Please clarify.

The reviewer is correct that ion counting systems are fundamentally limited by counting statistics. We have rephrased this to make the meaning clearer to the reader. The sentence is describing the general observation that at low mass to charge background peaks can be difficult to completely eliminate, and that the variability in these background signals (e.g. offgassing, impurities, etc) often limit the detection limits not purely sensitivity. At higher mass to charge ratios, the background often becomes negligible and improved sensitivity can be more readily realized for improving detection limits. These combined effects are readily visualized in an Allen variance plot measuring zero air.

**Figure S1.:** Unlike the rest of the examples, quantified data is reported herein. State how the data is quantified and/or show it in ncps.

The quantification information has been added to the figure caption.

Technical Corrections

**L13:** '*mass-to-charge of 381 (m/Q)*' - follow IUPAC guidelines (https://goldbook.iupac.org/terms/view/M03752): mass-to-charge of *m/z 381*.
Changed these all to m/Q Th.

**L45:** '*Decreasing the size and power of a TOF-CIMS…*': I assume the power consumption/demand is decreased.
done

**L46:** '*…the mass analyzer drift region…*': the mass analyzer's drift region
done

**L52:** '*The reduced target areas of these orifices reduces…*': The reduced target areas of these orifices reduce…
done

**L55:** repetition of the whole sentence "The reduced target areas... on the way to the mass analyser."
done

**L58:** change *power* to power consumption
done

**L66:** chang *hrs* to h following the IUPAC recommendations (https://goldbook.iupac.org/terms/view/H02866)
Done

**L69:** '*…mass resolving power…*': mass resolution. I assume a mass resolution at FWHM is used herein. Please clarify.
Done

**L76:** introduce AIM and PTR

We have added a brief introduction to PTR and AIM in the introduction.

**L77:** The year of the publication for 'Krechmer et al.' is missing (likely 2018). To introduce PTR-MS, cite the original work (e.g. Lindinger et al., 1997). No need to mention work in preparation for such an extensively studied instrument.

We have updated the references to include both the original work of Lindinger et al., 1997 and subsequent review papers on the PTR technique. The publication of Krechmer we feel is still relevant as in a compact instrument like is presented here, efficient ion focusing is critical to realize a compact high sensitivity version of a PTR instrument. The performance of this instrument is the subject of a separate publication (Claflin et al. in prep) but we agree that the above references are sufficient for this manuscript.

**L80 - L85:** There seem to be some inaccuracies. E.g. 'The instrument is pumped by dual…' Dual what? Introduce sccm together with 'standard cubic centimeters per minute' and not in L83. What are the '*otherwise standard flow conditions of (...) of ambient air…*'?

Done

**L86:** B+ is not used consistently throughout the manuscript. Often Bz+ is used. Select the more commonly used nomenclature.

Done

**L94:** '*..., held at, ...*': held at what?

Done

**L98:** '*The instrument achieves a mass resolving power of 1300 and mass accuracy of better than 10 ppm.*': This is a result that is also discussed in the result section. Remove it from the experimental section. Also: … and a mass accuracy…

Done

**L102:** '*... at a rate.*': At a rate of what?

Done

**L104:** introduce oVOCs

oVOC (oxygenated volatile organic compounds).

**L110:** a comma is missing after acids

Done

**L130:** '*...200W...*': 200 W

Done

**L145:** Table 1. Change Power to Power Consumption, stay consistent with units and use pptv instead of ppt. Also note the proper use of the term '*Mass Resolution*' in the table. However, m/delta m is not the unit of the Mass Resolution; it's the definition (m/delta m = 1300; like it is stated in Figure 3/c).

done

**L147:** The typical mass accuracy is a result. However, please clarify which m/z and which calibration function are used for mass axis calibration?

**L152:** '*MATLAB R2022b (The Mathworks, Inc., Matick, MA, USA)*': here the company is named together with its exact location. Compare to e.g. VACUUBRAND (L81) or Tofwerk AG (L75), where only the company is named. Please unify.
done
**L154:** for better readability, directly state the flagship VOCUS 2R as the commercial ToF-CIMS. Also: TOF-CIMS or ToF-CIMS? Introduced is TOF-CIMS (L32).
done

**L172:** Figure 2. add units to y-axis, xylene mixing ratio (ppt) -> (pptv)... needs to be consistent
done
**L183:** Figure 3. m/Q (Th) -> m/z, [C6H6]+ Mode to B+ or Bz+ (or any other consistent nomenclature); similarly for [I]- Mode.
done
**L189:** remove ')' at the end of the sentence; change '*...at m/Q less than 100 th*' to *m/z* < 100 (m/z is unitless according to IUPAC guidelines).
done

**L207:** the caption states HONO- instead of IHONO-
done

**L226:** '... of naphthalene C10H15O3)': add bracket. Also think of consistency. Is C10H15O3 in agreement with the otherwise used IC10H15O3- or the [IC6H10O5]- format used elsewhere in this manuscript.
done
**L248:** Figure 6/C titles IC10H5O3-, the caption mentions the C10H15O3 adduct with iodide ion. Figure 6/D titles IC6H15O5- but the caption mentions C6H10O5.
fixed

**Table S1:** add the unit of the concentration (I assume ppbv). What is the expected standard error of the stated concentrations? To my knowledge, all calibration gas suppliers state much more accurate concentrations than rounded to the nearest 100 ppbv).
The calibration gas standard is certified by NIST traceable measurements to +/- 5% accuracy, propagating the error of the multiple mass flow controllers required to reach a working concentration of 1-5 ppbv results in a total error of delivered concentration of <10%.

**Figure S1/b:** add a label to the y-axis, not only a unit
fixed
**Figure S2.:** add units to the colorbar; be consistent with the labeling (is it NH3+ or is it NH4C6H6+?).
fixed

References

Lindinger et al. (1997): https://doi.org/10.1016/S0168-1176(97)00281-4

Metzger et al. (2008): https://doi.org/10.5194/acp-8-6453-2008

Kramer et al. (2020): https://doi.org/10.5194/acp-20-5231-2020

Riva et al. (2024): https://doi.org/10.5194/amt-17-5887-2024

Aggrawal et al. (2025): https://doi.org/10.5194/amt-18-4227-2025

Song et al. (2026): https://doi.org/10.1007/s44408-025-00085-z

**RC2: (Orange)**

This paper developed and characterized the performance of a Portable-ToF-CIMS. This new lightweight and low-power instrument has high sensitivities and acceptable mass resolving power, allowing its great use in a range of mobile or stationary platforms for characterizing ppt level of trace gases. The authors demonstrate the performance of this instrument through short-period field measurements. This paper has important implications in atmospheric chemistry and air quality studies and therefore well within the scope of AMT. It can be recommended for publication after addressing the following comments.

Specific comments:

Lines 112-115: Can the authors provide more details on how calibration was performed, e.g., the number of data points? It looks to me that six different levels of standard gases were measured (Fig. 2a) while only four data points were used to generate the calibration curve (Fig. 2b). How would the calibration curve change if all data were included?

This calibration was performed using the four concentration steps as shown in Fig. 2b. At higher concentrations significant reagent ion titration is observed from our multi-component gas standard with nominal concentration of 1 ppbv. We have revised the figure to include the independently measured isotopes to extend the number of data points in our linearity figure and added the timeseries of the calibration experiment to the SI for clarity.

Line 133-135: How long would it take to power on the instrument and get a stable reagent ion signal?

Starting from a powered off state, the instrument takes about 15-20 minutes to acquisition startup. Establishing high vacuum in the TOF analyzer is relatively fast due to the much smaller analyzer volume. Ensuring the instrument is kept under vacuum when it is powered off, or it is filled with dry nitrogen helps ensure a fast startup time. The permeation tube also requires about 15-20 minutes to reach a stable operation temperature if starting from a typical room temperature of ~20 C. Our experience is that even in a non-ideal scenario a maximum startup time of about 30 minutes is routinely achievable. With vacuum established, voltages set and measuring is < 1 minute from off.

Line 166-167: The correlation coefficient of the fit should be given.
Done

Line 201-202: The authors stated that “The dynamic range (<1 pptv to > 1 ppbv), ppt-level precision and low detection limits of the instrument are evident.”. However, only normalized signals were shown in Fig. 5. The mixing ratios of these key pollutants should be provided.

Our approach has been to display ncps on the figures in the paper and then calculate expected sensitivities based on other studies and the calibrations that we did in our experiments. See below, in the paper and in the SI for more information.

Table S2: Measured and Calculated Analyte Sensitivities of the AIM reactor in $[I]^-$ mode. These sensitivities were reported in the literature for the AIM IMR operated at 50 mbar (Aggarwal et al., 2025; Riva et al., 2024; Wang et al., 2026). The AIM inlet in our experiments for the Portable-TOF-CIMS was operated at 100 mbar. A sensitivity in [I]- mode was experimentally determined for formic acid (CHOOH) and is shown in the table below as 8.4 ncps/pptv and is bolded. Using the ratio of this as the lower bound and the collision limited sensitivity as the upper bound we calculated the sensitivities of the AIM operated at 100 mbar for the other species we detected in these experiments.

| Analyte | Reported Sensitivity @50 mbar (ncps/pptv) | Calculated Sensitivity @100 mbar (ncps/pptv) |
|---|---|---|
| HONO | 6.5 | 22.0 |
| HNO3 | 15.0 | 30.0 |
| C2H4O2 | 1.0 | 3.4 |
| **HCOOH** | **2.5** | **8.4** |
| C6H10O5 | 15.0 | 30.0 |
| C5H10O3 | 15.0 | 30.0 |

Line 202-205: The morning peak of HONO started increasing at around 3 am. Is this due to automobile traffic or ground elements? Is the signal in Fig. 5b in units of ncps or pptv? If it is pptv, the HONO mixing ratio at noon time is high. Is this consistent with previous studies?

Thank you for pointing this out; the HONO is in ncps, and is now in a much more reasonable range in terms of mixing ratio.

Line 211-213: The maximum mixing ratio of HONO can reach 10 ppbv. It seems like a high value. What is the typical concentration of NOx in this area?

I believe this is addressed above by fixing the label for the HONO diurnal plot. Using transferred sensitivity for HONO, we found the mixing ratio maxima reaches ~60 pptv.

Line 224-227: Did C6H10O5 correlate with acetonitrile, another typical tracer of biomass burning? Mixing ratios should be given in Fig. 6, just like what the authors did for Fig. S1.

Acetonitrile can form a weak adduct with Iodide, but is typically better measured in positive ion mode. We used the collision limited rate for the quantification of Levoglucosan following Lopez-Hilfiker et al. 2016.

Line 236-238: Are there any other VOCs emitted from grilling detected, e.g., alkanals (Klein et al., 2016)?

We did not analyze these as the main goal of this paper was to simply assess portability and stability of the instrument.

Technical comments:

Line 16: Iodide and Benzene should be in lowercase.

Complete

Line 41: Spell out the full term of VOC and VCP. Check out the whole manuscript for similar issues.

I changed these at the intro, should be sufficient to introduce the terms.

References:

Klein, F., Platt, S.M., Farren, N.J., Detournay, A., Bruns, E.A., Bozzetti, C., Daellenbach, K.R., Kilic, D., Kumar, N.K., Pieber, S.M., Slowik, J.G., Temime-Roussel, B., Marchand, N., Hamilton, J.F., Baltensperger, U., Prévôt, A.S.H., El Haddad, I., 2016. Characterization of Gas-Phase Organics Using Proton Transfer Reaction Time-of-Flight Mass Spectrometry: Cooking Emissions. Environ. Sci. Technol. 50, 1243-1250.

**CC1:**

This manuscript describes an impressive portable CIMS. Because benzene cation is used as the reagent ion in this study, I would like to draw the authors' attention to our recent work[1], which focuses on benzene ion chemistry and has recently been accepted. It may be relevant to the interpretation of your measurements.

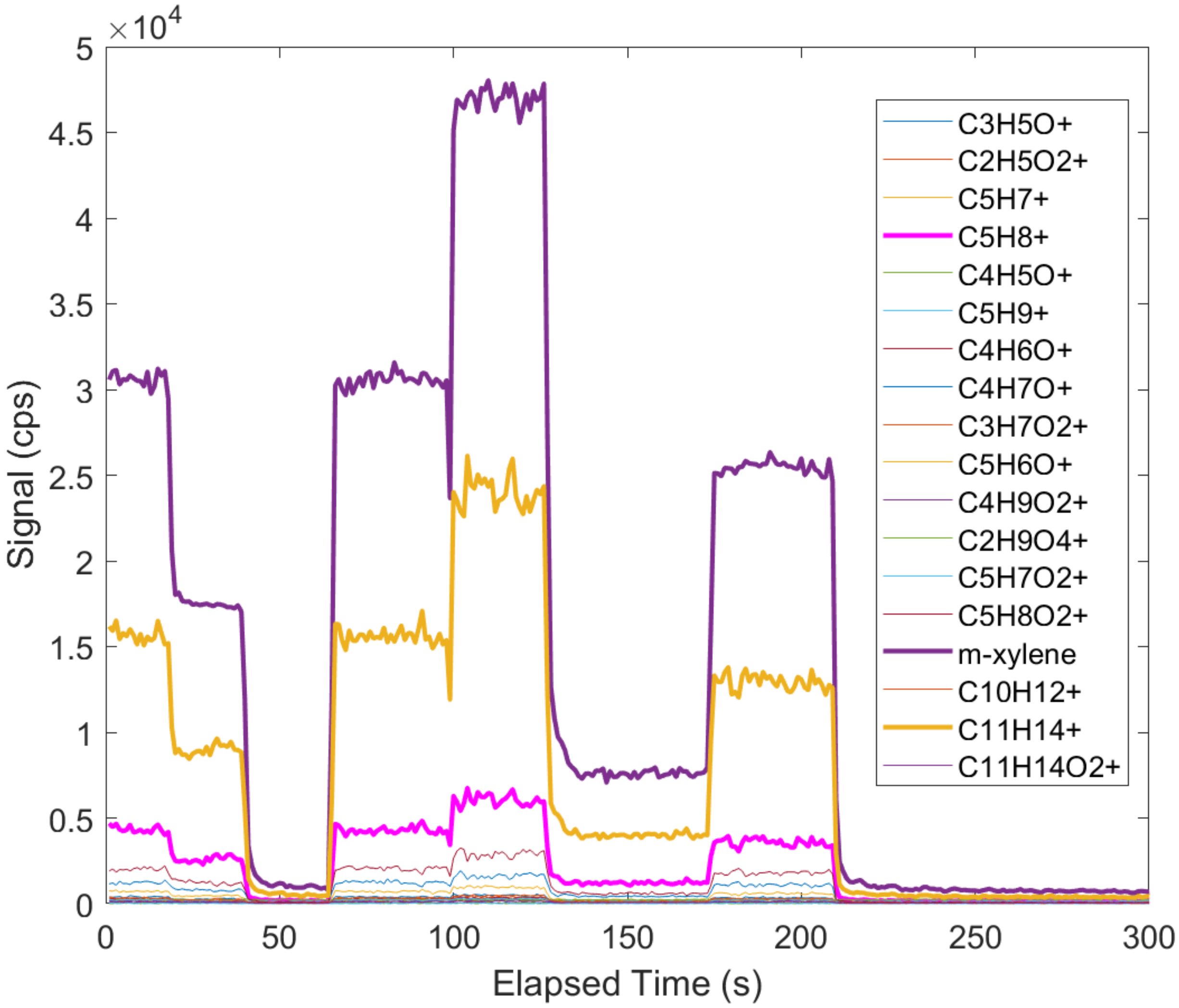
In our study, we observed several behaviors that were somewhat puzzling and I wonder whether you have observed similar phenomena. For example, during isoprene calibrations in zero air, we observed multiple fragment and oxygenated ions in addition to the parent ion ($C_{11}H_{14}^+$). I am curious whether a similar fragmentation pattern was observed in your experiments.

We also found a strong water-dependent sensitivity, which was challenging to correct using the measured water signal alone. I would be interested in your perspective on how this issue might be addressed when converting ncps to more meaningful mixing ratios. I fully understand that this question may be beyond the scope of the present study, but I raise it in the spirit of interactive discussion.

Lastly, I noticed a potential inconsistency between Figures 2A and 3A. In Figure 2A, the ratio of xylene to isoprene appears to be approximately 8, whereas in Figure 3A the same ratio appears to be closer to 2, assuming $C_8H_{10}^+$ and $C_{11}H_{14}^+$ are used to quantify xylene and isoprene, respectively.

We would like to thank Uma for their insight into benzene cation detection for isoprene. The calibration gas we used was diluted with lab air and so our measurements should be most closely related to the zero air measurements done in their paper. We evaluated the calibration data, fitting mass spectral ion peaks corresponding to the fragments mentioned in the Puttu et al. paper, except for known interferences at the mass channels corresponding to α-pinene ($[C_{10}H_{16}]^+$) and methyl-ethyl-ketone ($[C_4H_8O]^+$). We did not have a calibration standard containing only isoprene, and therefore cannot conclude that the masses fitted from the calibration and resulting signals are due to isoprene alone.

With the assumption that m-xylene is ionized mostly into the charge transfer product by benzene, it was used as a benchmark for the proposed isoprene fragments to assess whether we can close the gap between an expected (here, m-xylene) signal and "total" isoprene. At several different concentrations, it is evident that there are two major contributing factors (~70% of expected signal) from the charge transfer products and the adduct with benzene. The next two ions that contributed most to the expected signal are oxygenated products (like Puttu et al. suggest) with chemical formulas $C_5H_8O_2$ $C_4H_7O$. These species have responses in the timeseries data that clearly correlate with changes in calibration gas standards, indicating that isoprene is being reacted in this way, but further tests would be needed to determine whether there were other analytes being measured concurrently in our experiments. There are several mass-to-charge channels that fall below a 1% contribution to the "total" signal. These mass channels and minor products could very well be the signal that allows for experimentalists to "close the gap" between expected isoprene signal and measured isoprene signal. This discussion only applies to conditions where we are within a linear response range and not titrating the benzene reagent ion.


×10^4
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
Signal (cps)
0
50
100
150
200
250
300
Elapsed Time (s)
C3H5O+
C2H5O2+
C5H7+
C5H8+
C4H5O+
C5H9+
C4H6O+
C4H7O+
C3H7O2+
C5H6O+
C4H9O2+
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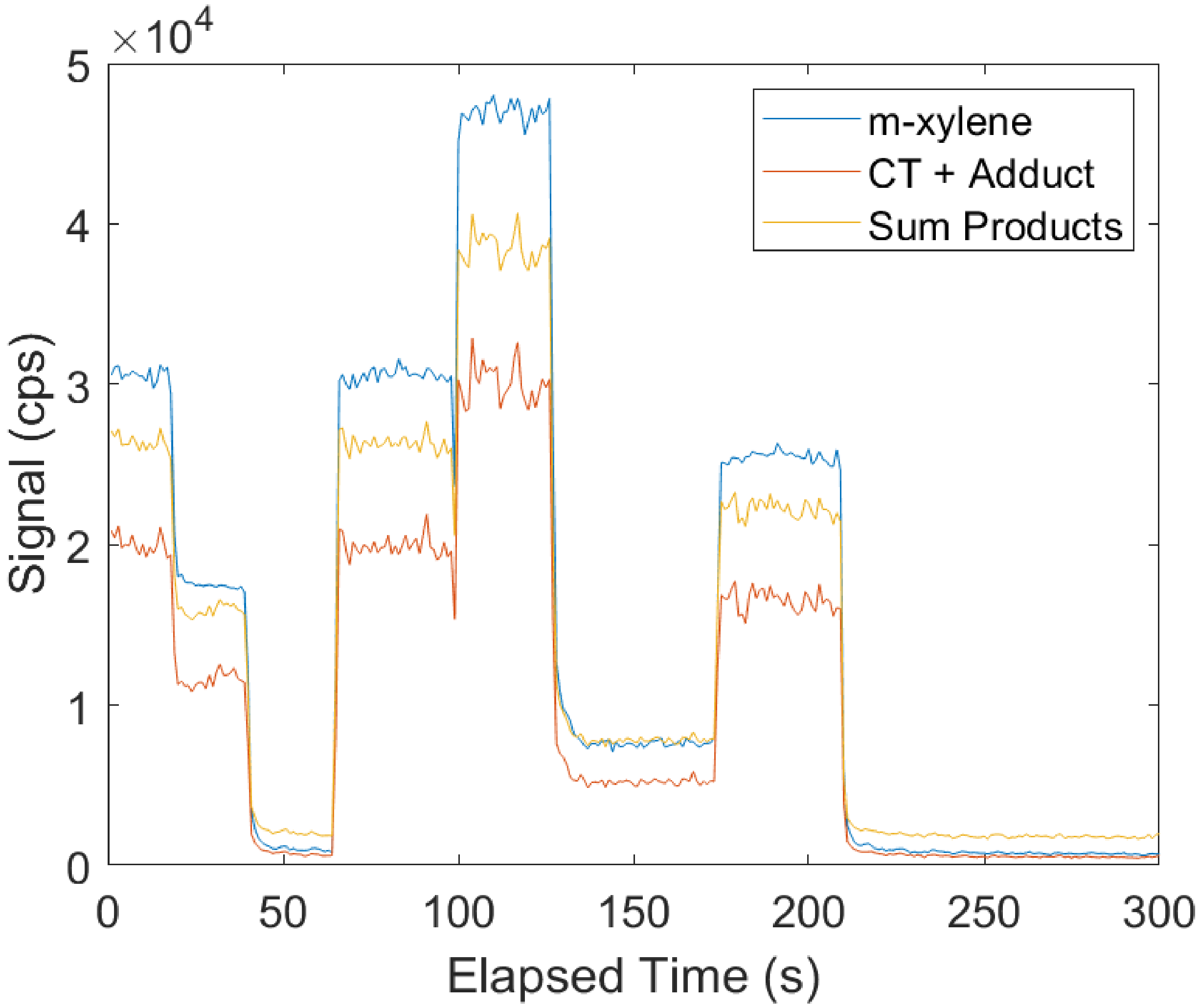
C11H14+
C11H14O2+


×10^4
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Signal (cps)
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200
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300
Elapsed Time (s)
m-xylene
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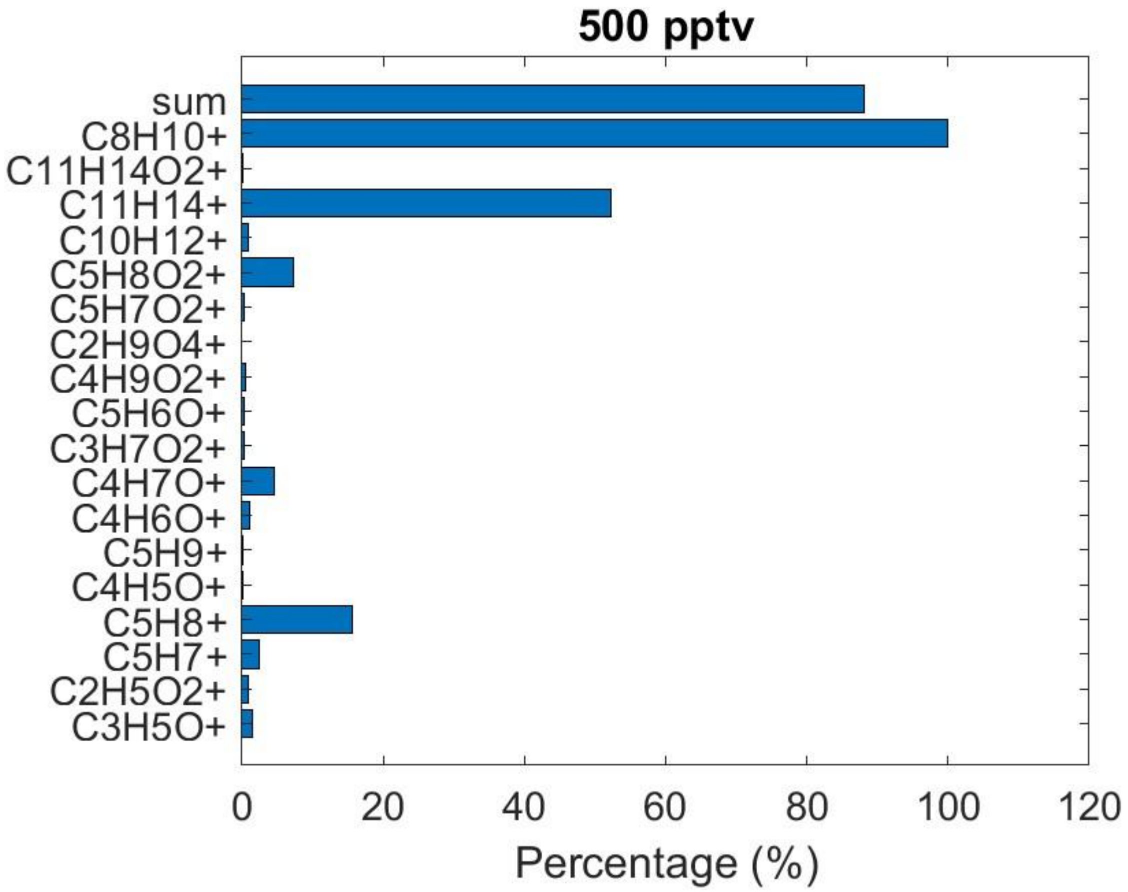
Sum Products



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