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

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AC: (black)

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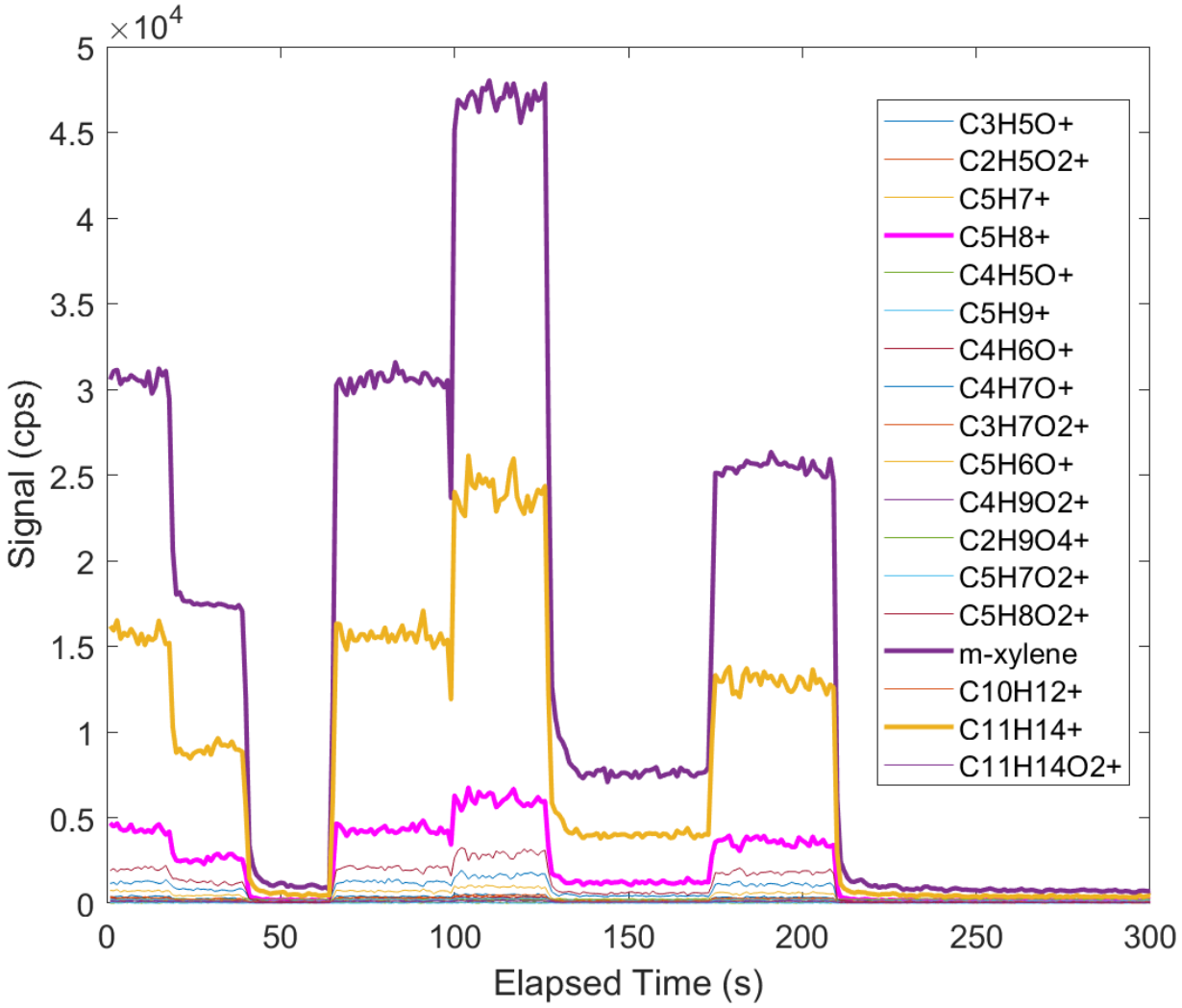
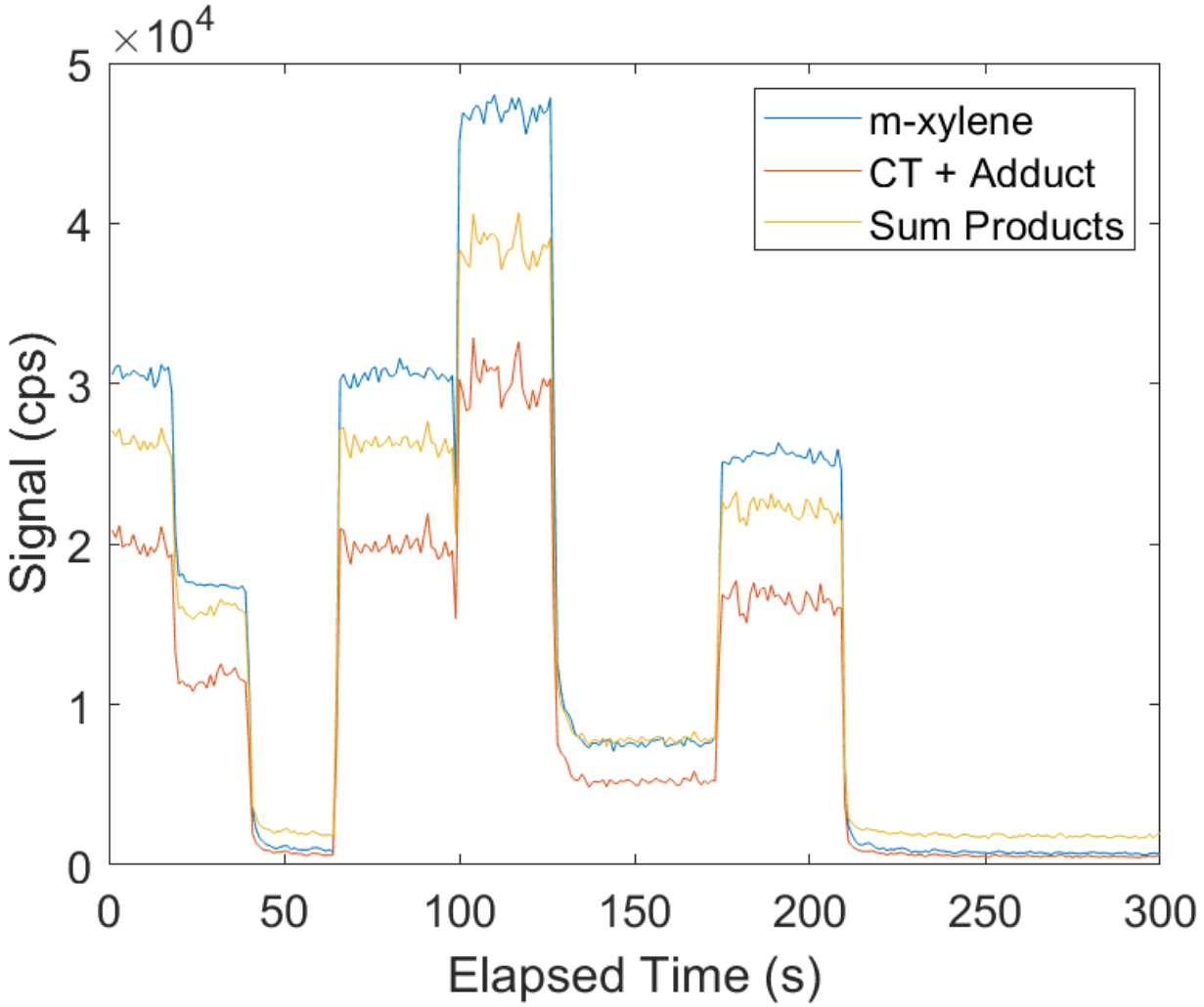
This manuscript describes an impressive portable CIMS. Because benzene cation is used as the reagent ion in this study, I would like to draw the authors' attention to our recent work [1], which focuses on benzene ion chemistry and has recently been accepted. It may be relevant to the interpretation of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

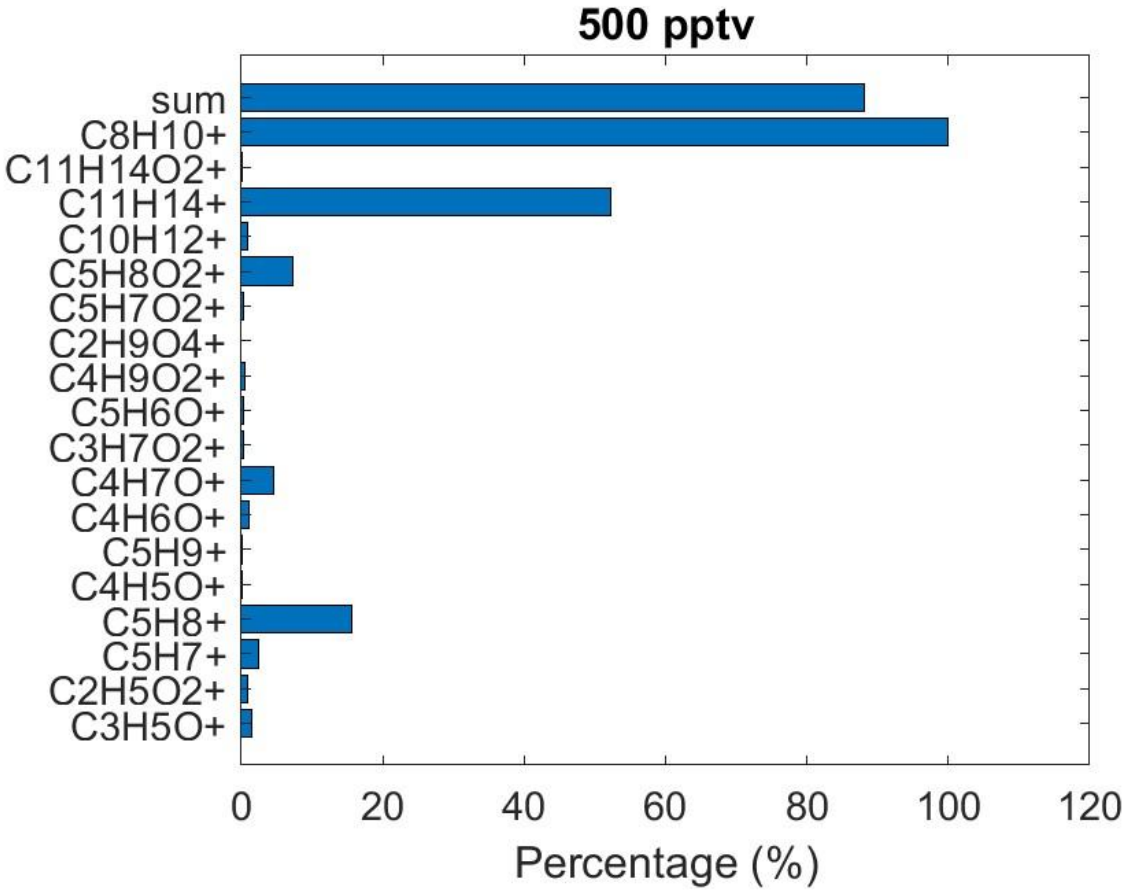
We would like to thank Uma for their insight into benzene cation detection for isoprene. The calibration gas we used was diluted with lab air and so our measurements should be most closely related to the zero air measurements done in their paper. We evaluated the calibration data, fitting mass spectral 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
3
2
1
0
Signal (cps)
0
50
100
150
200
250
300
Elapsed Time (s)
m-xylene
CT + Adduct
Sum Products



CC1 References:

1. Puttu, U., Kamp, J. R., Chen, X., Chen, J.-H., Li, J., Gonzalez-Meler, M. A., Wang, J., and Xu, L.: Chemical ionization mass spectrometry utilizing benzene cations for measurements of volatile organic compounds and nitric oxide, EGUsphere, 1–29, https://doi.org/10.5194/egusphere-2025-4103, 2025