

Interactive comment on “A high-resolution time-of-flight chemical ionization mass spectrometer utilizing hydronium ions (H_3O^+ ToF-CIMS) for measurements of volatile organic compounds in the atmosphere” by B. Yuan et al.

Anonymous Referee #2

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General Comments:

This paper describes the development and application of H_3O^+ traditionally used with quadrupoles to now commercially available time of flight mass spectrometers. The advantages of TOF compared to quadrupole mass analyzers has been described before in detail for many different ion chemistries and even the same ion chemistry as described in this manuscript.

This instrument of the instrument was deployed on the NOAA WP-3D aircraft as part of SONGNEX and its performance during the campaign was compared with other tradi-

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tional flight instruments. The manuscript is generally well organized and while it is not novel, is a thorough characterization of an instrument which will certainly participate in many flight and other measurement campaigns.

Ln 52 here and beyond the text could be shortened. The advantages of PTR with TOF technology are not new – and while it is useful to have the context of performance of other configurations, this may be better suited for the results and discussion section.

Ln 107 This is the same drift tube from the PTR-MS? If so this could just be stated, otherwise the differences to the commercial version could be highlighted.

Ln 137 If the instrument response is on the order of seconds what is the purpose of zeros for 90s? Is the response best described by a single or double exponential? Does the instrument (inlet, and instrument surfaces) not ever change on a timescale faster than the 40 minute zero frequency?

Ln 180 Given that the quadrupoles are now switchable on the TOF-CIMS with significant changes in the transmitted mass range it would be good to state what settings were used (frequency, amplitude, high-med-low coil)

Ln 217 It is not clear if the goal here was to optimize the sensitivity (i.e. to VOC alone) or also the reagent ions. As the reagent ions are likely heavily influenced by the mass transmission window of the quadrupoles it would seem like the absolute magnitude of the reagent ion signal should be of significantly less importance. Perhaps only optimizing VOC sensitivity is indeed what was done – if so then simple rewording would make this more clear.

Ln 225 (4) Discharge could easily be ruled out by turning off the ion source and measuring any residual ions of O_2^+ or VOC – It seems unlikely that at this pressure 80-100 V would lead to discharge.

Ln 243 The last sentence of this section (Ln 254 onwards) is more clear to me than the beginning of the section which seems unnecessarily long.

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Ln 427 This section seems to be just a demonstration of the resolving power which has been shown many times before – also for this same ion chemistry. What is new here?

Ln 448 Clearly the Quad version suffered from interferences that the TOF can separate, but this is not new, nor the fact that many ions are measured – I suggest either re-organizing this or removing this section as this has already been shown in previous publications.

Ln 485 Given the changing background signals – would shorter more frequent checks be more representative of the instrument background?

Ln 511 Can the fitting routine not also reduce the pure counting statistics by effectively fitting out the noise for well defined peaks? That is, for each point in the mass spectrum its signal is governed by counting statistics, but for each high resolution peak, many of these individual data points (in mass space) are fit. Therefore in the high resolution fitting procedure the individual counting statistics limitations can be “averaged out” by fitting, resulting in fit intensities which (at least for well defined peaks) are actually better than pure counting statistics would dictate.

Ln 537 While this is a nice plot, it is unclear why not just show the best quad sensitivity and the best TOF? Or what the point of the different measurements of quad sensitivities over time is meant to suggest?

Ln 555 This is repetitive, and is general knowledge that a quad has lower duty cycle for many compounds than a TOF. Once above in the introduction is reasonable but does not need later repetition.

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