

Interactive comment on “Evaluation of NO⁺ reagent ion chemistry for on-line measurements of atmospheric volatile organic compounds” by Abigail R. Koss et al.

Anonymous Referee #3

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General comments:

This manuscript presents a fairly straight-forward way to adapt a PTR-TOF mass spectrometer to use NO⁺ chemical ionization. It presents a comprehensive ensemble of experiments to establish the involved ion chemistry, and the methods employed. It also offers a thorough discussion of the results and the performance obtained, in particular in comparison to widely used PTR instrumentation. Furthermore, the results are very clearly presented (although I suspect there is still a bit of room for improvement). Therefore, I think that the manuscript is very well within the scope of AMT, and I believe it will be of high interest to the chemical ionization mass spec community. I recommend its publication, with a few minor revisions or clarifications.

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Specific comments:

Section 2 (e.g. lines 139+): How were the quadrupole ion guides set? As the authors state, these ion guides can change the measured ion distributions, e.g. via changing the m/z-dependent transmission, and adduct products can be more or less strongly de-clustered, directly affecting the presented results. (If one so desired, spectra could indeed be altered quite drastically.) So I wonder, was there any tuning done on the ion guidance elements, specifically for the presented experiments? Is it possible to compare the used quad settings with other conditions tested by the authors, or by others?

Table 2: Not totally clear to me, what the gray text means. The table caption says that gray is for additional product ions. "Additional" apparently meaning that they were not used to establish an NO⁺ sensitivity. I assume the last column texts are gray as well, because those detection limits do not directly relate to any of the numbers or formulas to the left. Or is there any relation to the other gray text? Could that be somehow presented in a clearer manner?

Sections 2 and 3.1.1-3.1.4 suggest that sensitivities (and simplicities) as well as reaction and fragmentation patterns were determined at dry conditions (I think that could be stated more clearly), whereas section 3.1.5 discusses humidity dependence. There seem to be some inconsistencies comparing some Figures and Tables. For instance taking MVK: Table 2B lists the product ions to be 100% C₄H₆ONO⁺ (m/z 100), but Fig. 2A, at operating voltages, shows that the product ion at m/z 100 (presumably C₄H₆ONO⁺) constitutes only ~70% of product ions. Other example, isoprene: Table 2A lists 46% of the signal as C₅H₈⁺, 17% as C₅H₈NO⁺, 7% as C₅H₇⁺, whereas Fig. 7B, at dry conditions, suggest >90% of the signal is C₅H₈⁺, <10% from C₅H₈NO⁺ and C₅H₉⁺ (not listed in Table 2, while C₅H₇⁺ is not shown in Fig. 7B). There is a similar discrepancy for benzene, where Table 2A doesn't agree with Fig. 7D, except maybe at about 20% RH... I may have gotten confused with the differences in experimental setup/conditions, or I understand Table 2 wrong? Either way, some clarification would

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be helpful, at least for this reviewer. Maybe by an additional table that summarizes conditions for each figure's/table's experiments?

Line 332: How long was a "measurement period"? And Section 3.2 in general: How did the zero measurements look like? Was the frequency of zero measurements sufficient? The frequency was once every hour for 3.2.2, but could not find out for 3.2.1 (see comment on line 332). I'd assume it was enough, but maybe show in supplement, by a figure, or by giving a few numbers.

Fig. S8 gives a glimpse at the challenges of TOF data analysis, in this case overlapping peaks, requiring "high-resolution peak-fitting algorithms" (line 422). I was missing some short statement on what software was used to tackle these and other challenges.

Line 141: "does not have that issue as strongly" is a bit too vague. I would prefer a more quantitative statement, or a suitable reference.

Line 354: I just don't get the message of this sentence into my head. I suggest the authors break it down or reformulate.

Technical corrections:

Line 11: "fast (sub 1-Hz)" ... To my understanding "sub 1-Hz" suggests slower than 1 Hz. Is "sub 1-Hz" what is really meant here, i.e. "up to 1 Hz"? Or the opposite, i.e. "1 Hz and faster"? The paper does present experiments at 1Hz and slower, but I would think faster (>1Hz) measurements would be possible as well.

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