

**Journal: AMT**

**Title: Evaluation of NO<sup>+</sup> reagent ion chemistry for on-line measurements of atmospheric volatile organic compounds**

**Authors: A. R. Koss et al.**

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**MS Type: Research Article**

**Response to reviewer 3**

**Reviewer comments are in black text.**

**Our response is in blue text.**

**Changes to the manuscript are in bold text.**

This manuscript presents a fairly straight-forward way to adapt a PTR-TOF mass spectrometer to use NO<sup>+</sup> 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.

**We thank the reviewer for their detailed and helpful comments. Replies to specific comments are below.**

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?

**The reviewer raises an important point that the ion guide elements can substantially change measured distributions of VOC ions. In particular, VOC·NO<sup>+</sup> adducts can be declustered by non-optimal ion guide settings.**

**At the end of this section (line 139+, line 171 in edited manuscript), we have added more explanation: "The two most important such adjustments decreased the electric potentials immediately upstream of each quadrupole ion guide (Figure S2). These adjustments reduced declustering at these locations, which improved the transmission of VOC·NO<sup>+</sup> clusters."**

**For transparency, and for readers interested in the details of the settings, we have added Figure S2 to the supplementary information.** This figure compares the ion guide voltage settings between the H<sub>3</sub>O<sup>+</sup> and NO<sup>+</sup> ToFCIMS. The optimal values of these voltages are instrument dependent, but the figure highlights the most important changes.

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<sup>+</sup> 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?

**We changed the color of the “H<sub>3</sub>O<sup>+</sup> CIMS detection limit” column to black and edited Table 2 caption to read, “Additional product ions not used to establish sensitivity are listed in gray text. The H<sub>3</sub>O<sup>+</sup> ToF-CIMS detection limits in the farthest right column are calculated from separate H<sub>3</sub>O<sup>+</sup> ToF-CIMS calibrations as described in Yuan et al. (2016)”. We also added a vertical line to visually separate the H<sub>3</sub>O<sup>+</sup> CIMS values from the rest of the table, which is exclusively NO<sup>+</sup> chemistry.**

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% C<sub>4</sub>H<sub>6</sub>ONO<sup>+</sup> (m/z 100), but Fig. 2A, at operating voltages, shows that the product ion at m/z 100 (presumably C<sub>4</sub>H<sub>6</sub>ONO<sup>+</sup>) constitutes only ~70% of product ions. Other example, isoprene: Table 2A lists 46% of the signal as C<sub>5</sub>H<sub>8</sub><sup>+</sup>, 17% as C<sub>5</sub>H<sub>8</sub>NO<sup>+</sup>, 7% as C<sub>5</sub>H<sub>7</sub><sup>+</sup>, whereas Fig. 7B, at dry conditions, suggest >90% of the signal is C<sub>5</sub>H<sub>8</sub><sup>+</sup>, <10% from C<sub>5</sub>H<sub>8</sub>NO<sup>+</sup> and C<sub>5</sub>H<sub>9</sub><sup>+</sup> (not listed in Table 2, while C<sub>5</sub>H<sub>7</sub><sup>+</sup> 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 be helpful, at least for this reviewer. Maybe by an additional table that summarizes conditions for each figure's/table's experiments?

This is a very helpful comment, because the discrepancies between product ion distributions reported in different sections of the paper are indeed due to different experimental setup/conditions, and some clarification is absolutely needed.

To clarify: The relevant difference in experimental condition was the relative humidity. In the laboratory, two relative humidities were used: dry air, and 20%.

The experiments done in dry air were: Adaptation of H<sub>3</sub>O<sup>+</sup> to NO<sup>+</sup> CIMS (Section 2.2, Figure 1, Figure 2). The 20% relative humidity is in the typical range of ambient relative humidity at our sampling site and time of year. By choosing a laboratory relative humidity condition similar to that expected for ambient conditions, it is easier and more robust to use the laboratory results to interpret the ambient data. The experiments done in 20% relative humidity or ambient humidity were: Laboratory experiments (Section 3.1, Table 2, Figures 3 through 6); and Measurements of urban air (Section 3.2, Table 2, Table 3, Figures 8 through 12).

How we have addressed this in the manuscript:

**In the description of each experiment, and in each table and figure, we have ensured there is a short statement of the humidity condition used.**

**At line 181: “A relative humidity of 20% was used for this experiment. This humidity condition is similar to that expected for ambient measurements discussed in Section 3.2; this condition was chosen to aid interpretation of ambient air data. Humidity effects are discussed in Section 3.1.5.”**

**At line 406: “The NO<sup>+</sup> ToF-CIMS was calibrated using air with ambient humidity (approximately 20%) for the 10 species listed in Table 2A, and no further humidity correction was applied.”**

**Table 2: ambient RH indicated for each section of the table.**

**Figure 1: Added “Experiment conducted in dry air (H<sub>3</sub>O<sup>+</sup> is from residual water in the instrument and in commercial ultrazero air.)”**

Figure 2: Added "Experiment conducted in dry air ( $\text{H}_3\text{O}^+$  is from residual water in the instrument and in commercial ultrazero air.)"

Figure 3: relative humidity 20% specified.

Figure 5: relative humidity 20% specified.

Figure 6: relative humidity 20% specified.

Figure 7B:  $m/z$  67  $\text{C}_5\text{H}_7$  added.

Figures 10, 11, 12: ambient air specified.

Figure S4: relative humidity 20% specified.

Finally, we have updated Table 2 to be entirely internally consistent: all  $\text{NO}^+$  sensitivities and product ion distributions reported here (in the revised manuscript) are now determined at ambient (20%) relative humidity. Originally, the sensitivities of the 11 compounds reported in Table 2A were determined in dry air, while all product ion distributions, and the sensitivities in sections 2B and 2C were determined in humid air. This was confusing and not indicated clearly. The new sensitivities in section 2A are calculated using data from multiple-step calibrations and background measurements conducted in air of ambient humidity (~20%). The revised limits of detection are not significantly different. **The revision to how limits of detection were calculated has been indicated at line 293.**

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.

"Measurement period" is the full three-day experiment. **To clarify, we have added the qualifier "three-day" to "measurement period" in all places where it appears in the manuscript. We also clarify that the 56-component standard was also used to determine instrument background on a daily basis (line 372).**

The background of the  $\text{NO}^+$  ToF-CIMS is of more interest to the CIMS community than the GC-interface CIMS. **To show the background of the  $\text{NO}^+$  ToF-CIMS, we have added Figure S10, which shows a time series of count rate, including background measurements, for several compounds.** The ion masses selected are  $m/z$  88  $\text{C}_3\text{H}_6\text{ONO}$ ,  $m/z$  71  $\text{C}_5\text{H}_{11}$ , and  $m/z$  78  $\text{C}_6\text{H}_6$  to show background for a range of functional groups,  $\text{NO}^+$  ionization mechanisms, and signal intensity. The zeros are clearly of sufficient frequency to establish background stability.

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.

**The name and manufacturer of the peak-fitting software (Tofware, from Aerodyne/Tofwerk AG), and a citation of a description of the algorithm (DeCarlo et al., 2006), have been added to the methods section in 2.1.**

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.

Modeled (expected) reagent ion distributions in the PTR-QMS -- based on ion energetics and relative humidity -- have been compared to actual, measured distributions, and the two distributions are quite similar (de Gouw and Warneke, 2007). Therefore, there is experimental evidence that the ion guides and

mass analyzer in the PTRQMS do not significantly change the reagent ion and cluster distribution. The difference between the two instruments is not surprising because the PTR-QMS does not have quadrupole ion guides, while the ToF CIMS does. **We have added a reference to de Gouw and Warneke (2007) with a short explanation at line 141 (line 143 in edited manuscript).**

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

What we meant by this statement is that we can identify ion masses that have contributions from multiple VOCs by comparing the NO<sup>+</sup> ToF-CIMS and GC-ToF-CIMS measurements. If an interference comes from a VOC that cannot be transmitted through the GC, then the NO<sup>+</sup> ToF-CIMS will measure a higher signal (the additional signal comes from the interfering VOC), and higher variability (if the GC-transmittable VOC and the interfering VOC are not perfectly correlated). **On reflection, this statement does not contain any useful ideas that are not already in this paragraph, so we have deleted line 354 (line 393 in edited manuscript).**

Technical corrections:

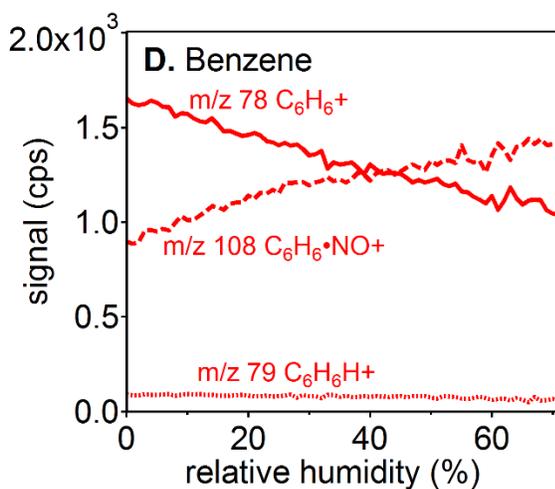
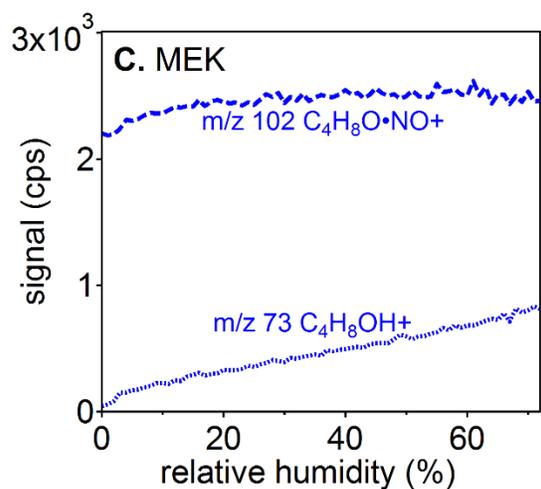
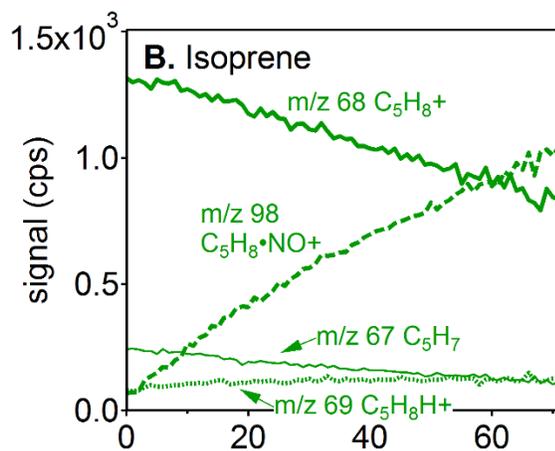
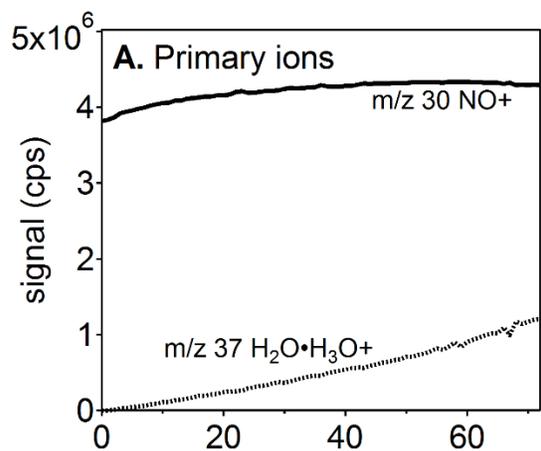
Line 11: "fast (sub 1-Hz)" ... To my understanding "sub 1-Hz" suggests slower than 1 Hz. Is "sub 1-Hz" what is really meant here, i.e. "up to 1 Hz"? Or the opposite, i.e. "1 Hz and faster"? The paper does present experiments at 1Hz and slower, but I would think faster (>1Hz) measurements would be possible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

The instrument is capable of measurements faster than 1 Hz, although we only present 1 Hz measurement here. **To clarify, we replaced "sub 1 Hz" with "1 Hz and faster" as suggested, and made similar edits elsewhere in the manuscript where "sub-" refers to measurement frequency.**

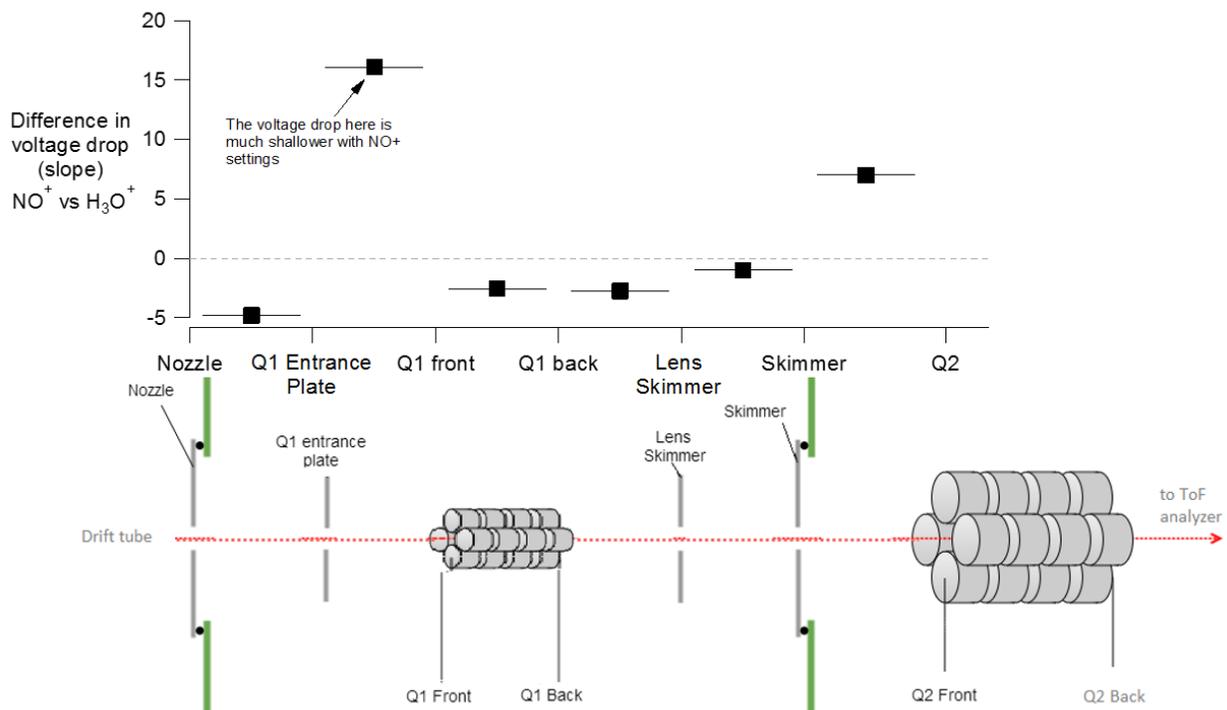
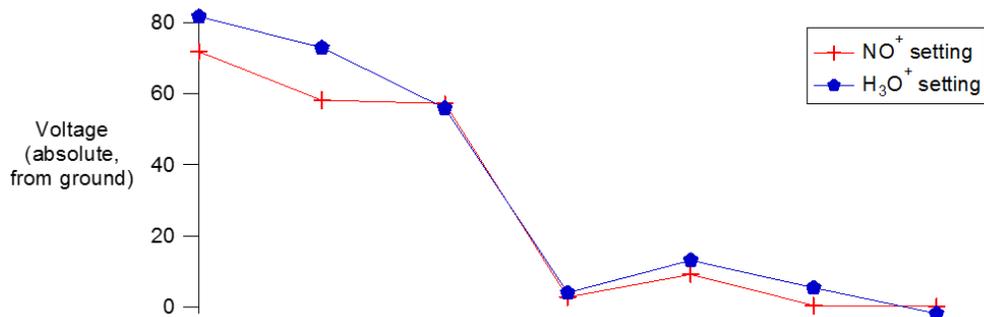
## References

de Gouw, J., and Warneke, C.: Measurements of volatile organic compounds in the earth's atmosphere using proton-transfer-reaction mass spectrometry, *Mass. Spectrom. Rev.*, 26, 223-257, 10.1002/mas.20119, 2007.

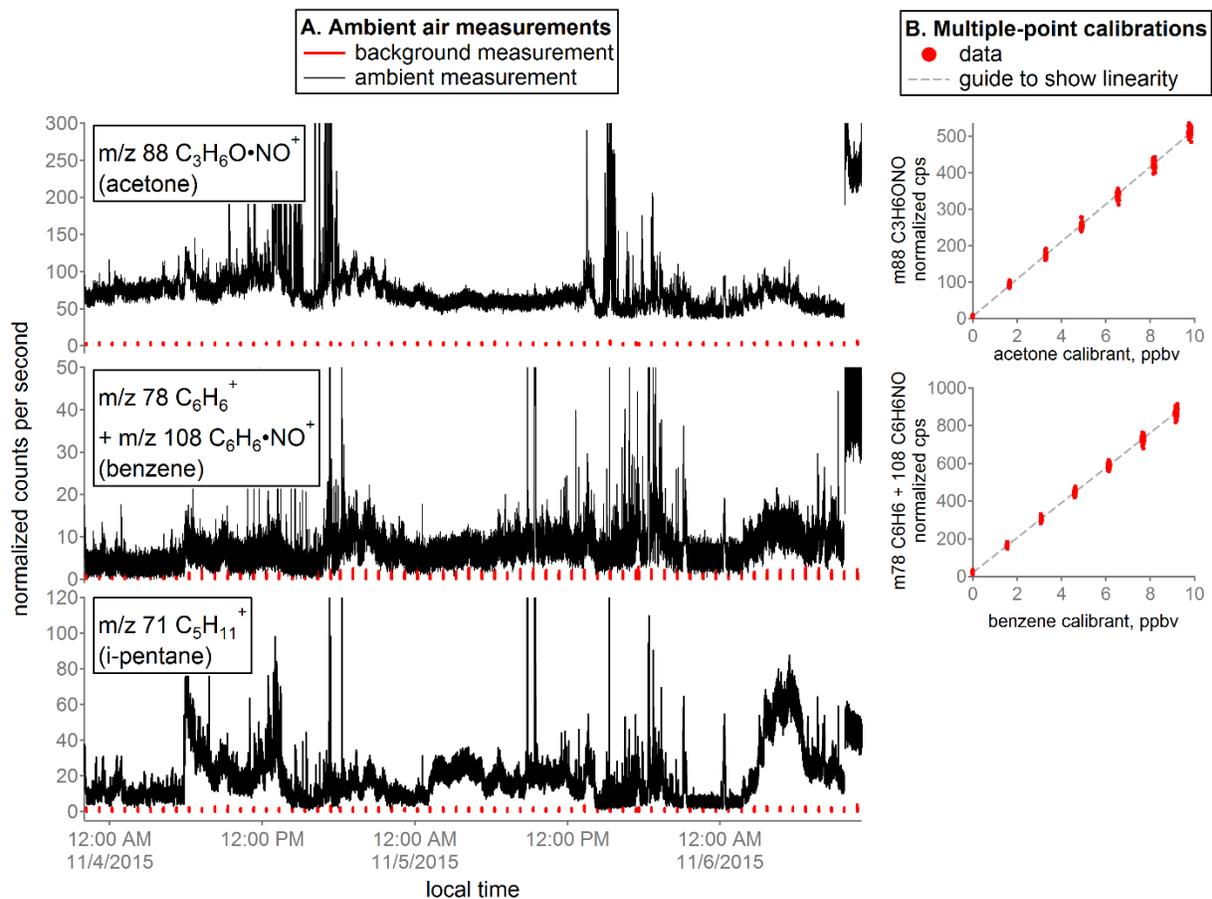
DeCarlo, P. F., Kimmel, J. R., Trimborn, A., Northway, M. J., Jayne, J. T., Aiken, A. C., Gonin, M., Fuhrer, K., Horvath, T., Docherty, K. S., Worsnop, D. R., and Jimenez, J. L.: Field-Deployable, High-Resolution, Time-of-Flight Aerosol Mass Spectrometer, 78, 8281-8289, 10.1021/ac061249n, 2006.



Updated Figure 7



**Figure S2. Ion guide voltage settings. The top panel shows the absolute voltage setting (from ground); the middle panel highlights the changes in voltage potential between  $\text{H}_3\text{O}^+$  and  $\text{NO}^+$  settings, and the bottom panel is a cartoon of the ion guide section taken from the CI-API manual (Aerodyne Inc./Tofwerk AG). The horizontal (axial) distances are not to scale.**



**Figure S10. A. Background and ambient measurements taken during urban air sampling with the  $NO^+$  ToF-CIMS. B. Example multiple-point calibrations of the  $NO^+$  ToF-CIMS showing sensitivity linear with concentration.**