

Interactive comment on “A high-resolution mass spectrometer to measure atmospheric ion composition” by H. Junninen et al.

Anonymous Referee #1

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This paper presents the development and characterization of a new instrument capable of mass spectrometric measurements of ion compositions. The authors present a brief characterization of the instrument, new analysis software tools for analyzing data from this instrument, and laboratory and ambient data. The paper is well written and suitable for publication in AMT after the following comments have been addressed.

General comments:

1. *More description of the instrument is needed.* As this is a new instrument more details are needed on the instrument itself, data collection and processing. The detailed characterization section of the paper lacks context on how exactly the instrument acquired and processed the data. Brief issues that need to be dis-

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cussed:

- How does the instrument record data, ADC or TDC (page 612 line 8 give an indication that TDC may be used, but it is not stated anywhere)?
 - If it is ADC, how is the signal converted to number of ions?
 - If ADC, Do ions give roughly the same signal as a function of m/Q ? As the m/Q range sampled in this instrument is quite large, this could be an important consideration in the ion transmission calculations in section 4.2
 - If TDC, how is the baseline / threshold set in the instrument?
2. *Mass Calibration and mass accuracy* The use of an empirical equation is not an issue for this application, but the particular empirical equation introduces a linear m/z parameter, which can have a pronounced effect on the mass accuracy of a calibration over large m/z ranges. Do the authors have a reference for this particular equation, or a justification of why it was used? Has it been compared with other empirical equations and given better mass accuracy? As the mass accuracy is not only a function of the mass spectrometer, but also a function of the data acquisition and mass calibration procedure, could the authors provide figures either in the text or as supplementary information demonstrating this. In both the abstract and in section 2.1 the mass accuracy is quoted, but no reference or demonstration of this is given in the paper. Are these simply the HTOF instrument specifications for the mass spectrometer? A characterization of mass accuracy for this paper would have an effect on the content of Figure 12, and is therefore interesting in the context of this paper.
 3. *Averaging and mass resolving power* Similar to the mass accuracy, the mass resolving power is a function of the data acquisition and processing as well as the mass spectrometer itself. From figure 11, it is clear that the averaging time has an influence on the width of the peaks (and therefore the mass resolution) with the 6 hour averaged peak broader than the 1 hour averaged peak. Longer averages

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will necessarily broaden peak width and decrease mass resolving power. Have the authors investigated this for their instrument? Is it possible, for example, that Figure 3 showing broader peak widths at larger m/Q could be due (at least in part) to longer averaging time for the ambient data compared to the calibration peaks? Is the mass resolving power measured for this instrument, or is it the mass spectrometer specification?

4. *Discussion on detection limit.* The discussion in the paper only the figure 6 caption gives any indication of the detection limit of the instrument. It would be important to have a section in the main part of the paper devoted to this. Additionally, the detection limit is given as $1e6$ molec per second or "roughly" 10^7 molec/cm^3 . From figure 5 it appears that this number is highly dependent on the ion transmission efficiency, which can be varied based on different instrument settings (figure 5). In light of this I would encourage the authors to discuss detection limit in terms of how many measured ions are needed per cm^3 for a particular S/N value. This could be followed by discussion of the ion transmission variability and how that affects the detection limits for different species in the instrument.
5. *Automatic Mass Calibration* The procedure for automatic mass calibration is quite interesting and not a trivial procedure to put together. One question that seems pertinent in this case, is whether the mass excess of hydrogen may have an impact on the second step of the described calibration procedure. From Equation 3, the baseline region that is minimized is from $X.3$ to $X.7$ with X being any integer above 10. From Figure 4, an ion with a m/Q of 410.47 is shown, which is in the middle of the baseline optimization region. While this is a calibration standard and ion identities are known, and one can avoid using the baseline optimization procedure, however for ambient samples with unknown ions, can the procedure reliably calculate accurate masses? It would be beneficial if the authors presented a comparison between using "known" peaks and a traditional calibration, and the method using the baseline optimization method. To validate

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the procedure.

Specific Comments (in the format Page/line)

604/2: Is there a reference for this equation? Has it been used in the past literature?

608/7-30: This method seems quite similar to the peak fitting algorithm implemented by the AMS analysis software, and described in DeCarlo et al. (2006). It would be appropriate to reference these here. Additionally, the use of a Gaussian does not seem appropriate given the peak shapes shown in Figure 7. Have the authors considered alternatives to a fixed Gaussian?

611/10 and 16: Here it is stated that no fragmentation of clusters happens within the APi-TOF, and later on line 16, you state that the fragmentation appears before entering the extraction region of the TOFMS. The latter statement is more accurate, since fragmentation post extraction can occur. It is suggested that the earlier statement (line 10) be reworded to be consistent with the second statement (line 16).

612/15 and 21: Could the authors elaborate on the dependence of voltage settings. Was any systematic dependence noted on ion transmission? What voltages showed the the strongest effects? Were the quadrupoles tuned, and how?

613/7: How is ion count per second determined? Some figures have axis legends in "signal" others in ion count per second, and others in ions / cm^3 . More details should be given for the reader to follow through all of the conversions.

617/6: Earlier it was stated that transmission was most sensitive to the APi settings, do the TOFMS settings also have a large impact here?

617/22: From figure 9 it appears that there are more black bars for ions less than 200 m/Q . This would be contrary to the statement that most of the atmospheric ions were identified, unless you are referring to total signal. In any case, the claim is ambiguous, and should be clarified.

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