

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

Anonymous Referee #2

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The following is a review of the manuscript entitled “A high-resolution mass spectrometer to measure atmospheric ion composition” by H. Junninen et al. This manuscript provides an overview of the APi-TOF, a commercial instrument for measuring ambient ions while also providing the possibility of adding an ionization source to enable neutral compound measurements. Overall I felt the presentation of the data was satisfactory (with the exception of the error made in the Kendrick analysis). My main comments relate to the presentation of the instrument and software. Overall I recommend publication after the following points have been addressed:

p601, In 10, please give the readers an indication as to the relative abundances of neutral species to charged, based on measurements. This is important because it gives some context as to the significance of the ambient ion measurement technique

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described here. A person not aware of the relative abundance of neutral molecules vs. ambient ions may not realize that the former far outweighs the latter based on observations by Eisele and colleagues. I note that on p615 this point is raised ... I suggest that this should be moved to this paragraph in this paragraph that starts on ln 7 since this issue of neutrals vs. ions is raised here.

p602, ln 25: Since the main purpose of this instrument is in “bridging the gap” between gas and particle phase measurements, it would seem appropriate to mention the m/z range of this instrument in this part of the document, along with some estimate of the equivalent mobility diameter range at large values of m/z .

p604, eq 1: the standard expression for mass to charge ratio is m/z . I suggest you use this here and in all subsequent references to this in order to reduce confusion. Eq. 4 can be left as-is, using a capital Z to denote the number of rings+double bonds.

p605, ln17: the threshold is mentioned here, but nowhere else. It seems to be an important aspect of the analysis worth mentioning. Normally such a threshold is defined as a function of the baseline noise (e.g., three standard deviations of the baseline noise). Please provide some discussion as to its significance in your analysis.

p606: Some additional discussion of equation 3 may be helpful. The calibration equation (eq. 1) describes the relationship between the flight time and the m/z of the ion. Given this, the only way that a and b can affect the baseline is if actual ions are in the region defined as “ion free” by the authors, that is, the 0.4 amu area between peaks. What was the basis for choosing this size for the ion free region? Are there any instances, when for example working with species with large mass defects like Fe or Si, in which this criterion may produce erroneous results? If this is a typical procedure for calibrating TOF spectra, can you provide a reference?

p605, ln 10: add space between 1-D and data

p607 ln10: please use a consistent notation: suggest Th.

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p607, In16: the correct expression for Kendrick Mass and Kendrick Mass Defect (according to all the papers that this ms references on this subject) are as follows:

$$\text{Kendrick Mass} = \text{Observed Mass} \times (\text{Nominal mass of CH}_2) / (\text{Exact mass of CH}_2)$$
$$\text{Kendrick Mass Defect} = \text{Nominal Kendrick Mass} - \text{Kendrick Mass}$$

The only place I have seen the expression used by the authors is in the Wikipedia entry on the Kendrick Mass. The authors must correct the text in this section, plus the data in Table 1 and Figure 12.

p607, In18: I feel that the authors should emphasize that the compound type (Z, also the number of rings+double bonds) can apply to any species type. The discussion provided here is specific to nitrogen-containing organics and, while it's obvious to those familiar with this analysis that it is generally applicable to CcHhNnOoSsPp... it may not be clear to everyone. This is especially important for the study of new particle formation, since sulfur and even halogens such as iodine may be important constituents of observed ambient ions.

p608, In 7: This paragraph belongs in the section on mass calibration. It only obfuscates the presentation of the Kendrick analysis technique, and does little to explain how exact mass analysis can be used for compound identification.

Interactive comment on Atmos. Meas. Tech. Discuss., 3, 599, 2010.

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