

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

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Answers to referee #1

General comments: 1. Referee has correctly noticed that we have not discussed the data acquisition. This is mainly because we have not developed software nor done any research on the topic. Instead, we have used manufacturer's software and routines to record the raw data. However, referee is correct, that little insight to data acquisition would be interesting for readers. The data can be recorded by using both, ADC or TDC. Which one will be installed by the manufacturer depends on application and use of the instrument. Our instrument was deployed originally equipped with ADC but soon changed to TDC. In general our signals are rather low and assumption, that for each extraction only single ions are recorded and each threshold crossing is indeed a single

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ion count, can be made. This is the reasoning behind, why we changed from ADC to simpler and cheaper TDC. But as for results and data interpretation there is little difference between these two, especially with our low signals. Most of the results presented here are measured with TDC.

ACTION: small chapter is added to discuss the data acquisition: Data was recorded using time-to-digital converter (TDC) by co-adding spectras for 5 seconds. Instrument was pulsed at frequency of 12kHz, which leads to 60000 co-additions in 5 seconds.

2. This equation is commonly used equation in time-of-flight mass spectrometry. Which is based on relationship between kinetic ( $E_k$ ) energy to mass ( $m$ ) and velocity ( $v=d/t$ ,  $d$ =distance,  $t$ =time):  $E_k=0.5mv^2$   $v=d/t=(2E_k/m)^{0.5} \Rightarrow t=d/2E_k^{0.5}m^{0.5}$   $d/2E_k$  – is considered constant (marked as  $a$ ), as  $d$  is flight distance of the ions that depends on physical dimensions (and running mode, V-mode has shorter distance than W-mode) of the MS and kinetic energy is energy given by pulsers, that is subject to change when instrument is tuned, but constant otherwise. This equation gives linear relationship between  $t$  and  $m^{0.5}$ , but since the ions are starting to move already when the pulse is rising an intercept ( $b$ ) have to be added to the equation.  $t=a*m^{0.5} + b$ , when solved for mass,  $m = ((t-b)/a)^2$  resulting the equation presented in paper equation 1. Other equations have not been used nor tested. We would like to use an equation as robust and rigid as possible and we think 2 parameters are minimum you have to use for a mass calibration and it is also sufficient when running in V-mode (mass resolving power 3000). At higher masses the resolving power is limiting factor not the mass accuracy. With higher mass resolving W-mode this simple equation might not be sufficient, but with W-mode also signal is significantly lower and noisier, so too flexible equation (with too many degrees of freedom) could lead to erratic results (over fitting). In this research all experiments were conducted in V-mode. The mass accuracy reported in the paper is from manufacturer specifications and we confirmed that this is a realistic value. We did not conduct experiment to define exact mass accuracy for each voltage set. Mainly this is due to lack of good calibration substances that would produce high number of

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known peaks throughout the mass range.

ACTION: none

3. will be answered in a next comment

4. In Figure 6 caption mentioning of detection limit of APi-TOF is actually misleading as it refers to detection of the whole experimental set-up used, that consists of nebulizer, charger, and APi-TOF. The reviewer is right, the reported detection limit is highly affected by ion transmission and ionization process and is therefore irrelevant in other application of the instrument, for example atmospheric sampling. The real power of the instrument is the atmospheric sampling without ionization in front and therefore the discussion about the detection limit of this one application was a mistake from our part. ACTION: mentioning of detection limit will be removed from figure 6 caption and chapter 4.3. New chapter and figure will be inserted

Fig 1. Detection limit of APi-TOF mass detector calculated from zero measurements of ambient air with ion filter in front. Detection limit is defined as 3 time standard deviation of individual raw spectras (15sec average). The instrumental background is extremely low and detection limit is from  $2e-3$  to  $6e-3$  ions/cm<sup>3</sup>.

5. will be answered in a next comment

Specific comments 604/2: See discussion in general comments point 2. For example Vorm and Mann (1994) used this equation to calibrate spectra, Guilhaus et al 2000 discussed about calibrating TOFMS in their review paper and also De Carlo et al 2006. Latter however set also the power 0.5 free and optimized with Levenberg-Marquardt algorithm. We however, did not want to have an extra degree of freedom, as our calibration peaks change from spectra to spectra and normally data is noisy an extra degree of freedom would introduce an additional source of uncertainty. ACTION: New references are added to the paper: Guilhaus, M., Selby, D. and Mlynski, V.: Orthogonal acceleration time-of-flight mass spectrometry, *Mass Spectrom Rev*19, 65-107, 2000

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Vorm, O. and Mann, M.: Improved Mass Accuracy in Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass-Spectrometry of Peptides, *J Am Soc Mass Spectr*, 5, 955-958, 1994

608/7-30: Referee is correct, the method is partly similar to the one presented in De Carlo et al 2006. Peak fitting routine has implemented a weighting that weights negative residuals (over fitted parts of the peak) and makes gaussian peak fitting insensitive to tail of the peak. This way the Gaussian peak fitting is suitable to use. However, we know that deconvoluting many overlapped peaks will have some extra uncertainty if fitted peak shape is not exactly matched with the actual peak shape. Additionally, in the latest version of tofTools the peak shape function (De Carlo et al. 2006) has implemented, but the presented analysis in the paper have done by using the older version of the software. ACTION: The reference is added to part where peak width vs.  $m/Q$  relation is discussed, as this is the most similar procedure of these two methods.

611/10 and 16: Referee has overlooked the details in the sentence on the row 10. We mean that no CONSIDERABLE fragmentation of THOSE clusters. So, our calibration clusters, not clusters in general. ACTION: none

612/15 and 21: This is very technical question and we feel that goes beyond the scope of the paper and interest of the readers. The information is only useful to owners of similar mass spectrometer with similar application (ionization/ion lenses etc.). However, as an answer, yes, the quadrupoles were tuned and they had the strongest effect on ion transmission. It is possible to tune the instrument in a controlled manner to be more sensitive to smaller or bigger ions. However, the bigger ions are less influenced by the voltage settings and have in general less signal anyway ( $mz > 1000$ ). Other voltages are not so critical for ion transmission point of view, but obviously have an effect for example on peak shapes and resolution. ACTION: none

613/7: Ion count units are: Ion count per second = Ion count per extraction \* extraction frequency (1/s) This unit was used in figure 6 where we compared APi-TOF signal to

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nebulized molecules. Reason is that amount of molecules nebulized was a known value, but the actual concentration at the instrument inlet was not known exactly, because of unknown ionization efficiency. Ions / cm<sup>3</sup> unit was used in context of ambient sample, this value is more relevant than ions per second. In figure 7 y-axis legend "Signal" is in units ion count per sec and the actual unit has left out by accident, we will add it to graph. ACTION: New y-legend in figure 7 617/6: This was bad phrasing from us. We mean voltage settings.

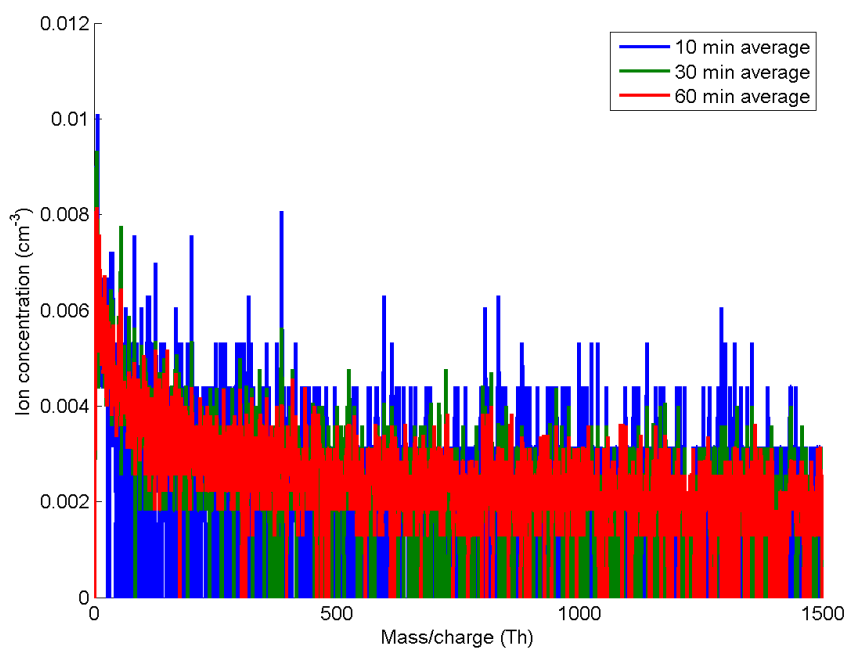
ACTION: rephrased internal settings -> internal voltage settings

617/22: Referee is correct the statement is not clear, we mean that most high abundance peaks are identified. ACTION: rephrased most peaks -> most high abundance peaks

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**Fig. 1.** Detection limit of API-TOF mass detector calculated from zero measurements of ambient air with ion filter in front. Detection limit is defined as 3 times standard deviation of individual raw sp

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