Review of “Furthering information from OH and HO_2+RO_2 observations using a high resolution time of flight mass spectrometer”

This manuscript is an instrument paper describing the advancement of a typical HO_xRO_x-CIMS instrument (i.e. Sjostedt et al 2007) by upgrading from a quadrupole mass spectrometer to a Time of Flight instrument (CI-APi-ToF). This change is mass spectrometer is a subtle yet important advancement for this type of instrument. Problems with duty cycle (the necessity of mass ”hopping” with a quadrupole) are removed and the entire mass spectrum can be measured with each acquisition. This provides additional information previously unavailable (or at least very difficult to obtain) with quadrupole instruments. The authors have shown a small amount of data at the end of the paper showing how the addition of SO_2, NO and propane (the OH scrubber) for the HO_x measurements perturbs the measurements of more large highly oxidized organic molecules (ELVOC, HOM’s). It would be nice to see this explored further (perhaps a part 2 of this paper)? The paper is clearly written and fits well into the scope of AMT. I recommend the paper should be published subject to a few minor comments below.

General Comments:

While the descriptions of the operating modes of the instrument (NO_3^-, OH, OH-Background, HO_2+RO_2, and HO_2+RO_2 background are detailed well, a little more detail about the operating conditions of the mass spectrometer would be appreciated (i.e. SSQ pressures, field strength used across the sheath/total flow lenses, ToF extraction frequency). While nitrate sources have been previously used on CI-APi-ToF instruments (i.e. Ehn et al 2014 and references therein), I believe a detailed account of the operating conditions is important as the HO_xRO_x front end does differ from the standard NO_3^- front end. Also how is the sheath air “filtered”, (charcoal scrubber?)? While backgrounds for OH and HO_2+RO_2 are discussed at length how is the background measurement for H_2SO_4 performed? Is simply inferred that the background count rates are 0 at masses 97 and 160 when there is no H_2SO_4 present? Presumably this background could rise if the sheath air wasn’t being scrubbed of adequately of ambient SO_2.

Specific Comments:

P2L30: The author’s refer to the mass spectrometer used in this instrument as an HR ToF while previously having called it a CI-APi-ToF. Please be consistent with the terminology so that those not in this community are not confused as to the mass spectrometer being used.

P3L20: Sjostedt et al also added HNO_3 through the CIMS rear injectors in addition to that added to the sheath gas to maintain the HNO_3 cluster distribution in the instrument. Was this found to be unnecessary with this particular inlet geometry? Does the cluster distribution change over time or even between operating modes? Does that effect the sensitivity? This is the type of information not available with a quadrupole system with a collisional dissociation chamber (CDC) designed to strip the clusters down to bare ions and certainly should be exploited with the ToF.

P4L17: The authors note that H_2SO_4 is detected at masses 97 and 160. Is the sum of the two used for quantification or only one of them? Please be clear.

P6L24: Are these detection limits for a 1 second measurement or has the data been averaged in post processing?

P7L14: The OH backgrounds shown in Figure 3 are high, due to the measurement being performed with unlabeled SO_2 instead of $^{34}SO_2$. I'm curious if the authors have a feeling about by how much the detection limit would be lowered (likely) by not having the measurement sit on top of a varying H_2SO_4 background. Of course whether this increase would be worth (the rather substantial) cost increase of using $^{34}SO_2$ would be debatable.

P8L15: Should be reactions R5 and R5a

P15: Figure 4. Since the data presented are 1 minute averages I think it would be useful to show the reader the standard deviation of the measurement so they can get a feel for the point to point variability as the count rates for the $C_{10}H_{15}O_8(NO_3^-)$ cluster are very low. In fact it's probably unnecessary to show 4 hours' worth of data. Displaying a smaller chunk of data would make the plot easier to read while still making the point that the $C_{10}H_{15}O_8(NO_3^-)$ cluster is anti-correlated with H_2SO_4.

P16: Figure 5: The same comment as above. It might be useful to stack the time series vertically as opposed to simply overlaying them on top of each other. The authors could perhaps put some type of shading in the background of the figure to denote when the instrument is switching between different modes.

References:

Ehn, M., et al., Mass spectrum of ELVOCs produce by a-pinene ozonolysis, Nature, 506, 476-479, doi:10.1038/nature 13032, 2014.

Sjostedt, S. J., Huey, L. G., Tanner, D. J., Peischl, J., Chen, G., Dibb, J. E., Lefer, B., Hutterli, M. A., Beyersdorf, A. J., Blake, N. J., Blake, D. R., Sueper, D., Ryerson, T., Burkhart, J., Stohl, A., Observations of hydroxyl and the sum of peroxy radicals at Summit, Greenland during summer 2003, Atmos. Environ., 41, 5122–5137, 15 doi:10.1016/j.atmosenv.2006.06.065, 2007.