Atmospheric Measurement Techniques Discussions

Interactive comment on "Organic particle types by single-particle measurements using a time-of-flight aerosol mass spectrometer coupled with a light scattering module" *by* S. Liu et al.

Anonymous Referee #2

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AMTD Review of Organic particle types by single-particle measurements using a time-of-flight aerosol mass spectrometer coupled with a light scattering module By Liu et al.

The paper presenting the results of single particle analysis from ambient data taken with an LS-TOF-AMS during the CalNex campaign is an important study, and certainly has some unique analysis that links bulk AMS measurements to the single particle measurements. Unfortunately, there are some major issues with the discussion of the paper as detailed below, mostly revolving around the ion counting issues, and the signal

to noise in the mass spectra due to those ion values. With the current discussion in the paper, and the fundamental issue with ion signal and the associated uncertainty with low ion counts in a mass spectrum, the paper cannot be accepted and must undergo significant reanalysis before it can be considered for publication.

Major Issues More detail is needed on how single particle mass spectra were generated including number of MS added together (i.e. was it the full chopper cycle, or only a subset of the chopper cycle). How were the Hz units calculated for Figure 5. If the Hz units were calculated using the chopper cycle time as the base time unit, then ion Hz signals need to be divided by chopper frequency (143 Hz) to obtain actual ions counted. Applying this calculation to Figure 5 it becomes unclear how there are 100 ions (stated as the detection limit for the procedure) in the average mass spectrum in parts a-c. The largest signals are approximately 280 Hz which when divided by 140 yield 2 ions measured in the mass spectrum, summing across the mass spectrum from 20 to 100 m/z, it is clear that there cannot be 100 total ions in the mass spectrum. If instead of the entire chopper cycle only a subset of the mass spectra for each chopper cycle were co-added for a 100 microsecond particle vaporization, then the Hz value in Figure 5 should be divided by 1000 (assuming 100 microseconds of data was added together) to get the number of ions at each m/z.

The following 3 excerpts from the paper reiterate the use of the 100 ion detection limit for analysis, which seems clearly at odds with the simple back of the envelope calculation of ions used for ionization efficiency calibrations included following the discussion.

page 3053 line 23-25 The detection limit, deïňĄned as the size at which particles produce detectable optical signals (S/N > 5) and chemical signals (>100 ions), was 180 nm dva (130 nm dg)

Page 3056 lines 2-4 The criteria of insignificant chemical signals includes a minimum sum of chemical signals for the mass intensity profile of 100 ions.

Page 3058 lines 14-18 The number of organic ions detected for each single particle is

a function of the organic mass fraction (for a given threshold of 100 ions described in Sect. 3.1) and particle size (larger particles produce more ions). Sulfate and nitrate, the major inorganic ions, were found to be independent of organic cluster types (Fig. 5), i.e., sulfate and nitrate, respectively, accounted for 16 percent and 4 percent of single-particle mass for each cluster (on average).

This calculation comes from the standard Ionization Efficiency calibration calculations. Details on this can be found in Allan et al. (2003) and Jimenez et al. (2003) Calculation of ions from a 108 nm (physical diameter) - Assuming ammonium nitrate:

Volume of particle: pi/6*d^3 = 6.59584e-22 m3 Molecules in particle (assuming density of AN at 1720 kg/m3 and Jayne shape factor of 0.8): 7.2e6 molecules of Ammonium Nitrate

Given an Ammonium Nitrate ionization efficiency of 2e-7 or 2 ions per 1e7 molecules (approximate for V-ToF-AMS), the number of nitrate ions one would expect from a particle 108 nm in diameter is: 1.4 ions of nitrate

Ammonium has a relative ionization efficiency that is roughly 4 times higher, but the ratio of NH4 to NO3 would reduce that by a factor of 3.4 so one would expect approximately 1.2x the ions for ammonium: 1.7 ions of ammonium

Total of roughly 3 ions or ∼30x lower than the assumed 100 ions for the lower detection limit.

One can easily calculate that the minimum diameter needed for 100 ions is quite a bit larger at: 343nm geometric diameter (keep in mind that ∼50 percent of these ions will be associated with ammonium (lower than 20 m/z) and not nitrate which will have 45 or so ions associated with it). Organic molecules have a lower density, and hence a lower mass per volume, and a lower ion generation rate, although their RIE is slightly higher. This means for an organic particle or one with significant organic material, the lower diameter limit for 100 ions will likely be higher than the 343nm needed for ammonium

nitrate.

Further, it is important to note that many of these particles are mixtures and are not pure components. This will further reduce the number of ions at a particular m/z especially if the material in the particle is organic which will spread the resulting signal over many more peaks in the mass spectrum (although a few key peaks will likely receive significantly signal).

Null calculations: If the threshold for a particle event is 100 ions, then how are null events determined? If a particle produces 50 ions that are clearly seen in the chopper cycle, is this deemed a null event and counted against the particle collection efficiency? How many ions are typically found at the "non-background" ions used in the mass intensity profile when there is not a particle present? All ions have backgrounds (look at the closed spectra of the MS mode), and a more complete analysis is needed here on the "average" non-particle ion count (Hz or absolute number of ions). This requires the saving of data from chopper cycles that do not have particles, and could also be compared to "null" particle events in terms of background ion signal.

Issue of particle coincidence: Have the authors considered the potential confounding issue of particle coincidence? If there is a 10 percent chance per chopper cycle that you sample a particle and save the MS data, then there is a 10 percent chance you will have coincident particles in those saved mass spectra. Do the authors have information on the number of chopper cycles saved vs number of total chopper cycles (as a function of time would be a bonus). This will give the reader an idea of the potential for coincidence.

Comparison to MS/PTOF data (non-SP data): The comparison of the PMF results to the clustering results is certainly interesting, and appears to have some good correlations, but the paper would benefit from more comparison with the MS and PTOF mode data. Specifically, on Page 3058 lines 14-18 (quoted above), were the values obtained for sulfate and nitrate, 16 and 4 percent respectively similar to the MS mode data for

the sulfate and nitrate mass fractions of the total? If not, perhaps the authors could speak to the differences, and the implications for internal vs external mixing.

References: Allan, J.D., J.L. Jimenez, H. Coe, K.N. Bower, P.I. Williams, and D.R. Worsnop, Quantitative Sampling Using an Aerodyne Aerosol Mass Spectrometer. Part 1: Techniques of Data Interpretation and Error Analysis, Journal of Geophysical Research – Atmospheres, Vol. 108, No. D3, 4090, doi:10.1029/2002JD002358, 2003.

Jimenez, J.L., J.T. Jayne, Q. Shi, C.E. Kolb, D.R. Worsnop, I. Yourshaw, J.H. Seinfeld, R.C. Flagan, X. Zhang, K.A. Smith, J. Morris, and P. Davidovits, Ambient Aerosol Sampling with an Aerosol Mass Spectrometer. Journal of Geophysical Research - Atmospheres, 108(D7), 8425, doi:10.1029/2001JD001213, 2003.