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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Single particle characterization using a light scattering module coupled to a time-of-flight aerosol mass spectrometer" *by* E. S. Cross et al.

Anonymous Referee #2

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Review of Cross

This manuscript describes some the first full analysis of field data with a light scattering module on a TOF aerosol mass spectrometer (LS-ToF-AMS). The work is very important and parts of it are excellent. However, the manuscript lacks focus and will need major revision to be published. The manuscript is very long; sharpening the focus will also naturally make it shorter.

The manuscript seems to have three different goals. The first is to analyze in detail what happens in the LS-ToF-AMS in a field measurement setting. This is the most important part of the manuscript. The LS-ToF-AMS offers some new capabilities to

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aerosol measurement. Since it becomes clear that ambient particles in some ways behave differently than laboratory calibration particles, the data are important not only for the LS-ToF-AMS but for everyone who uses any variety of an AMS instrument. The second goal is to compare the LS-ToF-AMS with laser ionization aerosol mass spectrometers. Although it is understandable for authors to be excited about their new instrument, these comparisons are somewhat biased and inaccurate. They therefore need to be eliminated or completely revised. The third goal is to describe the aerosols present during the deployment in Mexico City. There are some interesting nuggets but some of the assertions made are either speculative or fail the test of generalization: what happened during a few days of March 2006 at one particular location is not publishable unless it sheds light on more widespread behavior.

The first goal of the manuscript, analysis of optically triggered single particle data in a field setting, is very important. Strong points are that the manuscript provides some of the first direct measurements of bounce in an AMS and it provides quantitative data on the consistency of particle-to-particle ionization. The corresponding Figures 3 and 6 are very good.

There are three major omissions from the analysis of the optically triggered single particle data. First, the discovery of a delayed ionization mode is extremely important but is only given by a single threshold. Probability distributions of the delay (perhaps divided into optically small and large particles) should be shown.

Second, the algorithm for analyzing the mass spectra is not adequately described. After each light pulse, the instruments records 300 mass spectra. Somehow, these are averaged into a single spectrum and an ionization time determined. All we learn is on p 21327 line 3: "algorithms were developed..."; and "each m/z single of each single particle mass spectrum had separate baseline and signal-to-noise levels that required attention&". These algorithms need to be described as well as how you determined the baseline and signal-to-noise. The importance can be seen from data in Drewnick et al. (2005) when they ran a Q-AMS and a TOF-AMS side by side. The TOF-AMS

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measured an organic to sulfate ratio about a factor of 2 less than the Q-AMS. One possible explanation was that a threshold was set too high, so that many small organic peaks were eliminated whereas the sulfate signal, concentrated in a few strong peaks, was unaffected. If the choice of threshold can change data by a factor of two, it needs to be described in detail.

Third, there seem to be two major implications in this work for almost all previous AMS data. These need to be discussed. First, perhaps one third of the mass was from particles with delayed ionization. Yet delayed ionization is not apparent in laboratory data in, for example, Figure 6 of Cross et al. (2007) or Figure 4 of the original Jayne et al. (2000) paper on the AMS. It seems that ambient particles behave differently than laboratory calibration particles. If so, probably every published ambient AMS spectrum as a function of aerodynamic diameter, or at least every one in an urban area, is probably somewhat smeared in the x-direction. Is this true? Also, this manuscript shows some of the best evidence for particle bounce. The AMS is obtaining the composition of roughly half the particles, and it is very likely that the half that bounce do not have the same composition as those that are analyzed. What does this mean for the accuracy of AMS data?

Some lesser points about data analysis are:

- Figure 1 could use dimensions and Figure 2 needs to define which of several possible flight times is plotted (chopper to laser? laser to ionizer?).

- Figure 3 needs to clarify which flight time was used to define dva. If it is chopper to optical detection it is fine. If it is chopper to ionization, then a delayed ionization event not only moves a particle from the left to right panel but also moves it in the x-direction for a confusing comparison.

- Figure 4 should be eliminated: we find out elsewhere in the manuscript (p. 21333 line 26 ff) that in single particle mode the signal to noise is insufficient for the techniques shown for bulk mode in Figure 4. Since the focus of the paper is the single particle

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mode, Figure 4 is irrelevant.

- On page 21321 line 24 it is claimed that the single particle spectra can be analyzed with positive matrix factorization but on p. 21333 it says they don't have sufficient signal to noise.

- The discussion of the diameters and densities of the two sample particles (p. 21337) is unnecessarily complicated. There are three measurements (optical diameter, aerodynamic diameter, and total ion signal) and two unknowns (mass and diameter or density and diameter, as one chooses). There is therefore one internal consistency check. Figure 3 does a great job; all the discussion about derived diameters is just restating this in a more complicated fashion. In addition, there is one other check: is the derived density consistent with the chemical composition? This is stated clearly.

A second goal of the manuscript seems to be to compare, mostly in section 1.1, the new instrument to laser ionization instruments. As mentioned above, this section is biased. The easiest solution is to eliminate it completely, since the manuscript is too long to start with. Although it is easier to be quantitative when vaporization and ionization are separated, this section overstates the case. Some biases are:

- The abstract claims that the new instrument gives "single particle collection and quantitation" This statement needs to be qualified since quantitation is never established for the majority of particles (null and delayed events.

- Laser ionization instruments are criticized for having biased chemical detection, when due to bounce an AMS also has factor of 4 biases between common species such as ammonium nitrate and ammonium sulfate.

- Laser ionization instruments are criticized by saying that difficult to ionize species evade detection. This is not true for PALMS, which routinely gets mass spectra from over 90% of ambient particles that produce triggers, much better than the LS-ToF-AMS.

- Laser ionization instruments are criticized by saying that organic ions are fragmented

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to carbon clusters. This is not true for the ATOFMS, which has successfully measured PAH molecules with molecular weights over 200.

- Laser ionization instruments are criticized for inconsistent ionization. Yet by homogenizing the laser beam Wenzel and Prather (2004) demonstrated a variability in absolute ion intensity using a laser ionization instrument comparable to what the LS-TOF-AMS achieves.

- Laser ionization instruments are criticized because cluster analyses sometimes don't apply to mixed submicron particles. This is a straw-man argument: just because cluster analysis does not solve some data analysis problems does not mean that all analysis of laser ionization data is faulty.

The third goal of the paper is to describe some features of the aerosol chemistry in Mexico City. This section varies in quality from excellent to poor. As a general comment, the entire analysis comes from the 23% of particles that produced prompt signals rather than delayed or null signals. We know from laboratory work that the fraction of null signals depends on composition (e.g. from near 0% for ammonium nitrate to 75% for ammonium sulfate). It also seems that ambient particles produce more delayed signals than ammonium nitrate. Whether particles produce prompt signals or not depends on chemical composition. The subset of particles that is analyzed is therefore biased with respect to all particles. We don't know if this is a minor or major effect. The entire analysis needs to be done with this unknown bias in mind.

- The section on p. 21341 about mass closure should be rewritten or eliminated because the AMS is not accurate to anywhere near the 12% mass deficit that is discussed. As mentioned above, the results are based on a small, probably biased sample of the particles. The relative ionization efficiencies of different types of organic compounds vary by about a factor of 1.5 (Jimenez et al., 2003). The aerodynamic lens transmission contributes additional uncertainty whenever there is significant mass near the upper and lower cut points.

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- The section (4.3.1) on biomass burning particles should be eliminated because the conclusions are not supported by the data. First of all, it is possible that there were many more biomass burning particles but that they preferentially gave null signals. Second, the lack of a strong biomass burning factor does not prove that there was little biomass burning influence. It could also be that the mass spectral signature was not sufficiently distinct to fully separate it from HOA and OOA.

- The section on black carbon (p. 21346 lines 17 ff) should be eliminated because there are no data on black carbon from the AMS.

Section 4.4.1 on mixing state is in places excellent but in places ignores statistical significance. For example, on page 21350 line 15 it is noted that the fraction of intermediate-HOA particles containing NH4NO3 decreased after 12:00. Looking at Figure 12a, there were only about 20 intermediate-HOA particles measured shortly after 12:00 in total; an 80% fraction means that about 4 particles were detected without HN4NO3 during this time period. This is not very statistically significant. Other statements should be checked for statistical significance. The section on nitric acid equilibration with ammonium nitrate does not add to what is already in the literature on that subject. Section 4.4.2 on the SO2 plume event also does not add to the literature.

- The section on high chloride content is interesting. It would benefit from even a quick and dirty thermodynamic model calculation such as EQUISOLV or AIM showing the stability limits of NH4Cl under the conditions in the field experiments. Without it, you have evidence for NH4 and Cl occurring together but not specifically as the compound NH4Cl.

- The section on Pb should be greatly shortened. The criticism of laser ionization instruments possibly over-estimating Pb should be eliminated or limited to a factual statement about the relative sensitivity. With the current state of knowledge the laser instruments are actually more quantitative for Pb than an AMS, in which the relative sensitivity to Pb is unknown.

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