**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.

E. S. Cross et al.

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Responses to Anonymous Referee #2

We have identified 26 comments made by Reviewer #2 and labeled them alphabetically. These comments are listed below each with an associated response.

Comment A: 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 second goal is to compare the LS-ToF-AMS with laser ionization aerosol mass spectrometers. They therefore need to be eliminated or

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completely revised. The third goal is to describe the aerosol 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 in March 2006 at one particular location is not publishable unless it sheds light on more widespread behavior.

Response: The paper has undergone a major rewrite based on the suggestions from all 3 reviewers. The section 1.1 which had focused on comparing the LS-TOF-AMS with laser ionization aerosol mass spectrometers has been removed from the revised paper, as suggested here.

Comment B: 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.

Response: We agree with the reviewer that probability distributions are necessary to characterize the threshold for delayed versus prompt vaporization. In fact, the single threshold value used (200 us) was determined by plotting distributions of the chopper to chemical ion time-of-flight for each chopper to light scattering time-of-flight bin for laboratory-generated NH4NO3 and (NH4)2SO4 particles as well as polystyrene latex spheres. Distributions of chemical ion time-of-flights (for both optically small and large particles) revealed a composition-dependence to the vaporization/ion flight time. The 200 us threshold was chosen as an upper limit for prompt particle classification given the range of compositions expected in the ambient atmosphere. This has been clarified in the revised text, section 3.1, as follows.

Prompt particles are those that produced a chemical ion signal within 200 us of impacting the vaporizer surface. The timing of each single particle chemical ion signal measured with the LS-ToF-AMS contains two elements of timing uncertainty. (1) the uncertainty in the t0 due to the slit width of the spinning chopper wheel (1% at 130 Hz) and (2) the additional time it takes a particle to vaporize, be ionized, and de-

tected (called vaporization/ion flight time). The range of vaporization/ion flight times for NH4NO3 (80 us), (NH4)2SO4 (150 us) and PSL (200 us) particles serves as a rough guide for the range of vaporization/ion flight times expected for the ambient ensemble. Although not perfect, the 200 us upper limit for prompt particle classification ensures that particles that vaporize upon initial impact with the vaporizer surface are counted as prompt. Delayed particles produce a chemical ion signal > 200 us after the calculated arrival time at the vaporizer. Null particles do not produce a clear single particle chemical ion signal within the remaining PTOF time window (˜2.5 ms). In the MILAGRO study, the number fractions of the prompt, delayed, and null particles were 0.23, 0.26, and 0.51, respectively.

Comment C: Second, the algorithm for analyzing the mass spectra is not adequately described. After each light pulse, the instrument 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 signal 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 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.

Response: We agree with the reviewer, the algorithms for signal processing were not adequately described in the ACPD manuscript. We have moved the description of the data acquisition modes to Appendix A in the revised manuscript and additional details about the single particle data processing algorithms are outlined within Appendix A.3 as follows:

The LSSP mode of ToF-AMS operation is similar to the BFSP mode, except that single particle light scattering signals trigger the saving of chemical ion data. For every particle optically detected within a chopper cycle, the series of 300 mass spectra (300 spectra Œ 18 us = 5.4 ms PTOF time per chopper) and the light scattering signal for the complete chopper cycle are saved individually. Post-processing algorithms correlate each individual light scattering pulse with the integrated total chemical ion pulse (if any) that appears above the baseline (defined by the mass spectra that precede the particle arrival in PTOF time). As the single particle ion signals are typically small and exist on top of a constant background ion signal that is different for each m/z, m/z-specific thresholds are used to remove the DC off-set and reduce high frequency noise. Thresholds were set based on 3 x standard deviation of the background ion signal measured during the PTOF interval preceding the particle arrival at the vaporizer surface. Any ion signal that exceeds the m/z-specific thresholds provides a measure of the single particle chemical signature and is integrated to provide a total chemical ion signal as a function of PTOF time (i.e. 300 mass spectra). The maximum signal of the total chemical ion pulse is used to determine the timing associated with the single particle vaporization event (e.g. prompt, delayed, or null). Finally, the m/z-specific chemical ion signals are integrated across a window 0.612 ms wide to produce a single particle mass spectrum.

Comment D: 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.

Response: The reviewer correctly points out the importance of understanding the consequences of delayed (and null) vaporization on the interpretation of ensemble average AMS data. The original version of the ACPD manuscript did not discuss these details in a clear manner. As a result, in the revised manuscript we have restructured Section

3 on the single particle collection and detection of the LS-ToF-AMS. Specifically we have combined our discussion of prompt, delayed, and null particles with the ensemble average PTOF and MS data in section 3.3, entitled Single Particle and Ensemble Data Compraisons, to more clearly show the connection between the single particle vaporization event types, ensemble average measurements, and the mass-based collection efficiency.

The reviewer is correct in pointing out that Figure 6 in Cross et al. (2007), showing a monodisperse distribution of liquid oleic acid droplets, and Figure 4 in Jayne et al. (2000), showing size distributions of ammonium nitrate particles, both show only prompt particle vaporization events. As detailed in Matthew et al. (2008), both liquid oleic acid and, most likely, metastable ammonium nitrate particles are collected with 100% collection efficiency in the AMS. Thus, particles of these types exhibit prompt particle vaporization events. As shown in this paper, for the first time, particles with less than 100% collection efficiency exhibit delayed and null particle vaporization event types.

Comment E: 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?

Response: Yes. As shown in Figure 4a of the revised manuscript, the presence of delayed vaporization particles in ambient aerosol ensembles will tend to broaden the apparent size distribution of the particles toward the larger particle sizes. This is described in detail in section 3.3 of the revised paper.

The second observation is that the sampled ambient ensemble PTOF mode data (for the LS-TOF-AMS during MILAGRO) is broadened to larger particle sizes (dva) due to delayed single particle vaporization events. While this data set is not definitive, the comparison between the PTOF distribution and the LSSP prompt particle distribution

appears to indicate that the PTOF mass distribution mode is reasonably well represented (position and FWHM) and the delayed particle distribution creates a tailing to larger particles sizes that only significantly affects the large particle tail of the size distribution.

Comment F: 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?

Response: The reviewer focuses on an important point: Given the single particle observations of optically-detected particles that do not produce any measurable chemical ion signal, what does the LS-ToF-AMS teach us about the quantification/accuracy of the AMS data? We address this issue in the revised section 3.3, entitled Single Particle and Ensemble Data Comparisons. This section quantitatively compares the average, integrated LSSP mode signals with the average, integrated PTOF mode signals for total ion signal and for chemically-speciated ion signals. The PTOF mode signals are then quantitatively compared with the average MS mode total and chemically-speciated ion signals. Finally, a direct connection between the average MS mode signals and ambient particulate mass loadings and chemical compositions is made by referencing other detailed works that have directly addressed the CE issue. This analysis allows us to conclude that the different single particle vaporization event types do not result in a significant bias in the average nonrefractory mass concentrations and compositions obtained with an AMS.

Comment G: 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.

Response: Figure 1 has been revised with dimensions. Figure 2 is plotted with respect to the chopper to light scattering time-of-flights. The caption of the revised Figure 2 now states, Total particle counts (in grey) and number fractions of prompt (blue), delayed (green), and null (black) particles as a function of time-of-flight between the chopper and the light scattering module (bottom axis) and vacuum aerodynamic diameter (top-axis). The dva used in the Figure 3 was determined based on the Chopper-LS time (this has now been stated in the text).

Comment H: 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 mode, Figure 4 is irrelevant.

Response: We believe that Figure 4 in the ACPD manuscript is relevant to the description of the single particle results because we use the Principle Component Analysis (PCA) method to determine the single particle mass fractions of HOA and OOA. Therefore, it is important to show that the PCA method provides a similar result as the Positive Matrix Factorization (PMF) method for the ambient data set discussed in the manuscript. Note that Figure 4 of the ACPD manuscript is now Figure 5 of the revised manuscript.

Comment I: 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.

Response: This apparent contradiction is due to the fact that we did not clearly pointed out in the first statement that the single particle data are, in principle, amenable to more complex organic deconvolution techniques. The first statement has been removed, along with all of section 1.1 from the ACPD paper.

And the second statement now reads in section 3.4 of the revised manuscript

Our initial chemical analysis approach was to conduct PMF analysis on the ensemble aerosol mass spectra (MS Mode), ensemble PTOF distribution mass spectra, and single particle mass spectra. However, due to low S/N for signal at each m/z and low single particle counting statistics for the single particle data we have settled on the simple and published method for apportioning the organic fractions into two dominant components using m/z 44 and 57 (each with relatively high S/N) which have been shown to be the predominant signatures of distinct types of organics, labeled OOA and HOA, respectively (Zhang et al., 2005b). For the ensemble average mass spectra obtained in MS mode, PCA and PMF analyses are used to identify the different organic components.

Comment J: 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.

Response: We have shortened the section describing the measurements obtained from the coincident particles by removing the paragraph describing the time separation of the light scattering and chemical ion pulses. Rather than describing the calculations of the different parameters in detail, we have included calculation notes in Table 1, significantly shortening the section identified by the reviewer.

Comment K: 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.

Response: Section 1.1 from the original ACPD paper has been removed in the revised manuscript.

Comment L: 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).

Response: The abstract has been rewritten and the statement about quantitation has been removed.

Comments M-1 through M-5 address the need for a more accurate and fair comparison between existing laser-based SPMS instruments and the LS-ToF-AMS. As this section has been removed from the revised paper, our response here to these specific comments do not appear in the revised paper. Further, we will only address the AMS specific comments here, to avoid unnecessary confrontation.

Comment M-1: 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.

Response: The reviewer is correct that for pure, laboratory generated particles, the AMS exhibits a CE =1.0 for ammonium nitrate particles and a CE = 0.25 for ammonium sulfate particles (Matthew et al., 2008). It is worth noting that the CE for the AMS as determined in the field by direct comparisons with co-located instrumentation ranges from 0.45 to 1.0 (Canagaratna et al., 2007).

Comment M-2: 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.

Response: One of the key attributes of the LS-ToF-AMS is the spatial width of the triggering laser beam. In the case of the LS-ToF-AMS, the $1/e2$ width of the 405 nm

laser beam is ~ 2.7 mm to cover the downstream 3.8 mm diameter vaporizer (Cross et al., 2007) and the sampled, dispersing ambient particle beam (Huffman et al., 2005; Salcedo et al., 2007). The ambient particle beam was measured to ~1.6 mm wide at the 2 sigma level in Mexico City during 2003 (Salcedo et al., 2007). Thus, while this paper reports on only 23% of the detected particles, this was 23% of the total number of particles that passed through the aerodynamic lens and into the LS-TOF-AMS, which is an important achievement. The prototype system deployed during this study had a very low duty cycle, limiting the total number of particles detected and saved for analysis. Future versions of the LS-TOF-AMS have much higher duty cycles and will be able to save and process many more particles than the current system.

Comment M-3: Laser ionization instruments are criticized by saying that organic ions are fragmented to carbon clusters. This is not true for the ATOFMS, which has successfully measured PAH molecules with molecular weights over 200.

Comment M-4: 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.

Comment M-5: 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.

Comment N: 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

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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.

Response: The reviewer brings up an important issue concerning how the single particle measurements from the LS-TOF-AMS relate to the complete ambient aerosol ensemble. Section 3 of the revised paper provides a quantitative comparison between the LSSP results and the ensemble data (PTOF and MS), and connects AMS ensemble measurements to ambient particulate chemical composition and mass loadings. Section 4 of the revised paper has been restructured to clearly state the potential biases introduced by only analyzing in detail the promptly vaporized single particles. The comparison between the prompt single particles and the ensemble data for ambient measurements are discussed in some detail in section 4 to provide a more direct connection between the single particle data and the ambient aerosol.

Comment O: 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.

Response: This selection has been removed.

Comment P: 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

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was not sufficiently distinct to fully separate it from HOA and OOA.

Response: The ACPD section 4.3.1 has been eliminated as a separate section. As other recent literature results from the MILAGRO study have noted a strong biomass burning influence and a PMF factor that represents a marker for biomass burning organic aerosol (BBOA) is found in the ensemble MS data, we discuss biomass burning particles in the revised version in section 4. Within this discussion, we discuss the differences between the ensemble and single particle BBOA markers and clearly state the possible reasons for under-counting biomass burning single particles based on our analysis of only the promptly vaporized single particles.

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

Response: The section has been removed.

Comment R-1: 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 NH4NO3 during this time period. This is not very statistically significant.

Response: In Section 4 of the revised version of the manuscript we have removed the text and figures associated with statistically questionable results. Overall, section 4 has been placed in the context of the statistical limitations of the initial deployment of this new instrumental method.

Comment R-2: 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.

Response: The section on nitric acid equilibration has been removed.

Comment S: Section 4.4.2 on the SO2 plume event also does not add to the literature.

Response: We disagree with the reviewer on this point. The SO2 plume observation shows a point source emission with gas-to-particle condensation on all measured prompt single particles. We have, however, demoted this discussion from a separate section (section 4.4.2 in ACPD paper) and incorporated it into the revised section 4.1.1. entitled, Trends of internally mixed aerosol species.

Comment T: 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.

Response: We agree that using a thermodynamic model with the ambient conditions at T1 during the period of study would help confirm the presence of NH4Cl, though this is out of the scope of this paper. Its worth noting that while not definitive, Figure 13 in the revised paper (Figure 14 in ACPD) shows mass balance in prompt single particles between the NH4 and Cl measured, supporting our contention that these particles are composed of a significant fraction of nonrefractory NH4Cl.

Comment U: 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.

Response: We have removed statements addressing the quantification of laser ionization instruments from the paper and this section.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 21313, 2008.

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