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Comment

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 Referee #1

Reviewer 1 has made 42 comments. In the original file, the reviewer listed his/her comments A-Y. Where necessary we have subdivided the reviewer's comments so that each individual comment has a response. Reviewer Comments are shown in italics. Author responses are shown un-italicized.

General Comments: the reviewer's comments raise three issues: (I.) Inaccurate presentation of the current laser-based SPMS systems (II.) Inadequate discussion of collection efficiency details obtained with the new LS-ToF-AMS system. (III.) Over-interpretation of the ambient data set due to statistically limited sampling.

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Full Screen / Esc

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Interactive Discussion

Discussion Paper



Response: The paper has undergone a major rewrite based on the suggestions from all 3 reviewers. We have removed section 1.1, which had focused on comparing the LS-TOF-AMS with laser ionization aerosol mass spectrometers. We have rewritten section 3 to better explain the single particle vaporization events and how they relate to the collection efficiency of AMS instruments, as suggested by this reviewer. And, we have rewritten section 4 to emphasize the useful information obtained with this new instrument configuration (prompt single particle information combined with ensemble data) within the limitations of the first deployment of this prototype system.

We respond to each specific comments raised by the reviewer below.

Comment A-1: On p. 21319, it is stated: "Perhaps even more importantly, the organic ions generated from most laser-based aerosol mass spectrometers are highly fragmented, in many cases to the point of formation of carbon cluster ions. Such fragmentation limits obtainable chemical information (e.g. C:O ratio, organic species) " - This statement is incorrect. The extent of fragmentation of single particle mass spectrometers strongly depends on the laser desorption wavelength used.

Response: The sentence about organic ion fragmentation in laser-based SPMS instruments has been removed.

Comment A-2: On p. 21319, it is also stated that nitric acid is not detected with single particle mass spectrometers. This is incorrect. Nitric acid has a strong absorption cross section at 193 and 266 nm and thus readily detectable.

Response: We have removed the statement about nitric acid detection.

Comment B: On p. 21321, it is stated: "While clustering techniques have proven useful at identifying trace components that may point to particle sources (e.g. metals), it has yet to be shown that laser-based instruments and their clustering analysis techniques can provide quantitative measurements of the composition and mixing state of ambient submicron aerosol particles, which are composed mainly of non-refractory organic,

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sulfate, and nitrate species." - This statement is erroneous as it ignores many articles in the published literature. Using calibration procedures, a number of publications have shown single particle instruments can indeed obtain mass concentrations as well as quantitative information on particles. Many relevant papers on various aspects of quantification of signal from single particle mass spectrometers can be found using a relatively quick literature search on Web of Science.

Response: The section on clustering techniques has been removed from the revised manuscript.

Comments C-1 through D2-7 address the topic of AMS collection efficiency and pose questions about how the single particle results can be used to better understand the standard AMS mass quantification procedures. Overall, we agree with the reviewer the single particle data can improve our understanding of the collection/detection efficiency of the AMS by providing insight into the extent and nature of the vaporization/ionization process for particles within the optically-detected size range. While more work must be done to elucidate the details of this process, initial insights about these issues that are provided by this study have been reorganized and are now discussed in more detail in section 3. Specifically, section 3.1 describes the single particle vaporization event types, their number fractions of the total particles sampled, and their temporal and size-dependent behaviors. Section 3.2 compares the chemical ion signals measured for each single particle vaporization type with single particle mass estimated from independent do and dva measurements. Finally, section 3.3 compares the summed single particle chemical ion signal measurements with the average ensemble PTOF and MS mode measurements.

Comment C-1: p. 21328: The paper states that over the 75 hour sampling period, 49% of all optically detected particles produced a measurable ion signal. It would be interesting to show how much this % varied over the entire study. The average is not nearly as useful or informative.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Interactive
Comment

Quinn et al (JGR, 2006) have recently shown the CE for the AMS varies over time as a function of chemistry and RH. In the study by Quinn, they used a RH controlled inlet (at relatively high RH) so their ability to detect ammonium sulfate was higher than the value reported in this paper (0.54 vs 0.25). For this reason, it would be worth noting the range of RH variations during the study in this paper. Response: We agree with the reviewer that a continuous time trace of the fraction of prompt, delayed and null particles is a necessary step toward unraveling the complex issues of particle collection and detection within the AMS instrument. A graph containing these time traces has been added to figure 2.

With respect to the reviewer's question about the role of relative humidity, the relative humidity during the period of sampling ranged from a high in the overnight and early morning periods of 80-85% to a low of 15-20% during the middle of the afternoon each day. The fraction of single particles with prompt vaporization did not appear to change during periods of high/low relative humidity.

With respect to the reviewer's comments on the mass-based CE determined and reported for the LS-TOF-AMS in the ACPD version of the manuscript and the rewritten version of this paper, the reviewer incorrectly suggests that we reported a CE = 0.25 for sulfate measurements during this project.

Comment C-2: Also, if the CE is varying over time and one uses a constant CE, how much error does this introduce into the results? In particular, if you are using sulfate as your proxy for the fraction of the total mass of the aerosol the AMS detects, and it only detects 25% for ammonium sulfate, then the masses for all chemical species (even organics) are multiplied by this same factor of 4? If the organics (such as aged SOA particles) occur in more liquid-like particles, wouldn't this result in an over-scaling of organic mass? A useful application of the light scattering tool and a nice addition to this paper would be to discuss whether when the overall CE is low, if more externally mixed particles (less aged particles) are present. This could be an incredibly useful diagnostic for understanding the ambient aerosol as well as the quantitative potential

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for the AMS.

Response: In this study the LSSP mode was used to identify and measure the total number and number fractions of single particles that displayed prompt, delayed, and null vaporization events. This is a particle number based measurement in a narrow particle diameter size range ($dp > 250$ nm). The AMS CE that the reviewer has mentioned is an empirical scaling factor that accounts for less than unit mass detection efficiency of ensemble nonrefractory mass concentrations obtained from the MS mode. Since the LSSP mode and the MS mode have significant differences in the measured particle size range, measurement timescale and the use of particle number vs nonrefractory particle mass, the LSSP prompt, delayed, and null number fractions measured during this campaign cannot be automatically converted into a CE value for the campaign. In fact, during this campaign the prompt, delayed, and null particle number fractions were 23, 26, and 51% respectively and the AMS CE for this campaign was 0.5 NOT 0.25 as incorrectly stated by the reviewer. The reviewer's apparent misunderstanding of the connection between the LSSP mode measurements and the insights they provide about the AMS CE indicates the need for a better discussion of these points in the manuscript. Thus we have included a new section (3.3) that compares the Single Particle, PToF, and MS mode data. The text that is relevant to the reviewer's comment is excerpted below:

As the MS mode represents the most complete collection of available chemical ions, ambient mass concentrations are derived from MS mode and subsequently scaled by an empirical collection efficiency (CE) factor (Jimenez et al., 2003; Alfarra et al., 2004; Quinn et al., 2006; Matthew et al., 2008). For ambient AMS measurements, the CEs range between 0.45 and 1 (e.g. Canagaratna et al., 2007, and references therein). The nonrefractory mass-based collection efficiency of the LS-ToF-AMS during MILAGRO was determined to be ~ 0.5 by comparisons with co-located SMPS-derived apparent mass distributions and black carbon measurements, and with direct comparison with a C-ToF-AMS deployed in the Aerodyne mobile laboratory during a two day visit to

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



the T1 site (Herndon et al., 2008). A mass-based CE of 0.5 has also been determined and verified independently by several other groups that have deployed AMSs to Mexico City during MCMA-2003 and MILAGRO, including Salcedo et al. (2006), Johnson et al. (2008), Kleinman et al. (2008), DeCarlo et al. (2008), Paredes-Miranda et al. (2008), and Aiken et al. (2009). The LS-TOF-AMS data presented in this paper provides direct evidence that the mass-based collection efficiency of the AMS is a result of particle bounce. The nonrefractory mass for prompt single particle vaporization events is collected with near unit efficiency while delayed and null particle events contain mass that is undetected on the PTOF timescale. The AMS mass-based CE = 0.5 for this campaign indicates that 50% of the nonrefractory particulate material sampled is not detected, even in the longer MS mode timescales. Since refractory species account for only 20% of the submicron ambient PM in Mexico (Querol et al., 2008; Aiken et al., 2009; Salcedo et al., 2006; Chow et al., 2002), these observations strongly suggest that the non-unit mass-based CE in this campaign is a result of delayed/null single particle vaporization events during which nonrefractory material was not completely detected.

Comment D1: In Figure 2, it shows for most sizes the null particles represent almost 70% of the total particles yet they report a value of 51% on average. This size dependence seems very important to incorporate. The authors go on to use 23% of the particles which are biased towards the smallest sizes even though only 10% of the larger, more massive, particles are detected. Figure 2 would be more informative if the x-axis showed particle size instead of time of flight.

Response: Figure 2 of the ACPD manuscript referred to by the reviewer, is perhaps not as clear as it could be. In accord with the reviewer's suggestion, we have added an additional x-axis to the top of the graph indicating the vacuum aerodynamic diameter of the particles detected. We have also added a trace to the plot that shows the fraction of the total single particles found in each size bin. The information displayed in Figure 2 now shows that the largest size bins contain $\sim 1.6\%$ of the total particles sampled.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

To illustrate the range of sampling statistics across the different size bins, error bars have been added in Figure 2 to the fraction of prompt and null particles. The error bars indicate that the size dependence of particle collection may not be as severe as initially indicated in the ACPD manuscript.

Comment D2-1: p. 21329: In the MILAGRO study the number fractions of the prompt, delayed, and null particle events were 0.23, 0.26, and 0.51, respectively. The prompt particles contained 59% of the total measured single particle mass, whereas the delayed and null particles contained 38% and 3%, respectively.

This is a confusing and potentially misleading statement. More details on how these values were determined are needed. Is this just derived from the total ion signal in other words, are the authors saying that prompt particles form 59% of the total ion signal measured in the AMS?

Response: We agree that these statements are confusing without more context. In the re-written Section 3.3, the comparison between the LSSP measurements and the PToF measurements are outlined in more detail.

Comment D2-2: Again, it would be interesting to know the % of the actual aerosol mass the AMS is accounting for with these 23% of the particles it ends up analyzing. For example, one could compare the AMS mass results with another mass-based technique such as the PILS-IC or filter methods there were many filter-based methods being used during MILAGRO. Another recent paper reports PILS nitrate measurements during this same period:

Hennigan, C. J., A. P. Sullivan, et al. (2008). "On the volatility and production mechanisms of newly formed nitrate and water soluble organic aerosol in Mexico City." *Atmospheric Chemistry and Physics* 8(14): 3761-3768.

In Figure 3, the particle mass obtained from ion signal is shown versus the mass obtained from the particle diameters. Notably, this is a log-log scale and significant scat-

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tering is still obvious presumably due to chemical differences in the ambient aerosol. This is another reason it would be informative to compare the total mass calculated from the AMS with a non-AMS mass measurement for PM₁, such as filter-based method, to determine what fraction of the total ambient PM mass is actually being detected at different points of the study. Comparisons could be made during periods with more prompt vaporization vs. delayed vaporization vs. null events to better understand the chemistry of the particles during these different periods.

Response: We believe that Figure 3a (Fig 4a in revised manuscript) does a reasonable job showing the percent of the total aerosol mass we measure on a particle by particle basis for the promptly vaporized particles. In connection with the request for a comparison between the AMS and another mass-based measurement, we believe that we have completed this through our comparison of the AMS and SMPS methods as described in the original text and through comparisons with several other AMSs deployed in Mexico City :

The non-refractory mass-based collection efficiency of the ToF-AMS in which the LS unit was installed during MILAGRO was also determined to be ~ 0.5 by comparisons with co-located SMPS-derived apparent mass distributions and black carbon measurements, and with direct comparison with an C-ToF-AMS deployed in the Aerodyne mobile laboratory during a two day visit to the T1 site (Herndon et al., 2008). A CE of 0.5 has also been determined and verified independently by several other groups that have deployed AMSs to Mexico City during MCMA-2003 and MILAGRO, including Salcedo et al. (2006), Johnson et al. (2008), Kleinman et al. (2008), DeCarlo et al., (2008), Paredes-Miranda et al. (2008), and Aiken et al. (2009).

One of the goals of subsequent work with the LS-ToF-AMS will be to complete careful comparisons of the mass measured with the LS-ToF-AMS (within the optically-detected size range) to total mass measurements obtained with other instruments. One complicating factor in such comparisons is that most of the ensemble, total mass measurements are not done in a size-specific manner. To obtain accurate comparisons of the

LS-ToF-AMS single particle mass measurement, the total mass measurement must be adapted to the optically-detected size range. Such comparisons are outside the scope of the current manuscript.

Comment D2-3: An important question relevant to the atmospheric chemistry community is how do the finding in this paper impact ensemble AMS mass calculations and quantification?

Response: The findings in this paper provide the first direct insight into the vaporization/ionization process inside the AMS. A new detailed discussion of the connection between the LSSP mode results and the PToF and MS Mode ensemble mode mass calculation can be found in section 3.3.

Comment D2-4: What are the assumptions in the ultimate AMS mass calculations if the AMS is only detecting 23% of the particles? What is the error introduced by the original assumption that the AMS is detecting every particle and the ones being detected are fully representative of the atmosphere?

Response: This is a very important issue. We believe that there is some misunderstanding reflected in the comment of the reviewer. We will try and clarify the issue here in this response and stress it more clearly in the manuscript. As stated in the original manuscript, the 23% is the fraction of the total particles with prompt ion signals at the vaporizer. Ion signals in the mass spectrometer are produced by both prompt and delayed particles. The sum of these two makes up 49% of the total sampled particles by number. When measuring ensemble average mass concentrations of non-refractory ambient aerosols both prompt and delayed vaporization contribute to the total ion signal measured in the mass spectrometer.

The original assumption of the AMS is that it provides a representative average measurement of the non-refractory mass concentration and composition in the atmosphere. Ambient mass concentrations are typically derived from MS mode, and then scaled by an empirical collection efficiency (CE) factor (Jimenez et al., 2003; Alfarra et al., 2004;

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Huffman et al., 2005). For ambient AMS measurements the CEs derived from inter-comparisons to a large number of total PM and speciated instruments range between 0.45 and 1 (e.g. Canagaratna et al., 2007, and references therein). Previous publications have shown that for any given study, a single AMS CE factor not only reproduces the total mass but also the speciated mass to within +/- 20% (e.g. Drewnick et al., 2003; Hogrefe et al., 2004; Takegawa et al., 2005; Zhang et al., 2005a; Quinn et al., 2006) and also the fractions of different types of organic species (Zhang et al., 2005c; Takegawa et al., 2006; Kondo et al., 2007; Docherty et al., 2008; Aiken et al., 2009). This suggests that the different vaporization modes do not result in a significant bias in the average non-refractory mass concentrations and compositions obtained using the MS mode.

Comment D2-5: What is the range of values for the CE, as determined using the light scattering signals, over the course of the study?

Response: As discussed in the response to comment C2, the LSSP mode measures the total number and number fractions of single particles that displayed prompt, delayed, and null vaporization events. This is NOT the same as the AMS CE which is an empirical scaling factor that accounts for less than unit mass detection efficiency of ensemble non-refractory mass concentrations obtained from the MS mode. Thus, the results of the LSSP measurements cannot be used to address questions about the range of values of CE. However, if the reviewer is asking about the variability in number fractions of prompt, delayed, and null single particles, then we refer them to the time trends in figure 2a.

Comment D2-6: "A linear fit to the data in Fig. 3b has a slope of 0.41 ($R^2=0.12$), suggesting that the measured chemical ion signals represent only about 40% of the total particle mass. Given the extremely poor fit to the data and large scatter (R^2 only equals 0.12) as well as the large size bias shown in Figure 2, it is a significant stretch to conclude the AMS is detecting 40% of the total particle mass.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Response: We agree with the reviewer that the scatter in Figure 3b (Figure 4b of the revised manuscript) is rather large. Nevertheless, this figure does illustrate that the particle mass measured by the mass spectrometer when compared to the calculated mass from the diameter measurements is significantly smaller for the delayed particles than for the prompt particles (displayed in Figure 3a). We believe that this is a real and significant observation. We have re-phased our discussion of Figure 4b as follows in the text:

The data obtained from the delayed vaporization events are shown in Figure 4b. This set of data exhibits significantly larger scatter and lower overall chemical ion signals than obtained from the prompt vaporization events. A linear fit to the data in Figure 4b has a slope of 0.41 ($R^2 = 0.12$), indicating no clear correlation between the two measurements and suggesting that the measured chemical ion signals from delayed particle vaporization events generates a significantly lower percentage of the total single particle mass than that of prompt events. Some of the reduced signal may be due to the presence of refractory components in these particles. Also these values likely only correspond to the measurement timescale of the PToF mode. As discussed in section 3.3, on average, 25% more of the delayed particle mass may be detected in MS mode where the measurement timescale is three orders-of-magnitude longer.

Comment D2-7: For many particles (51%), the AMS is not detecting any mass at all. p. 21329: "produced a measurable chemical ion signal while the remaining 51% did not produce a clearly detectable chemical signal. This count-based collection efficiency is close to the mass-based collection efficiency of 0.5. However, we note that the count-based and mass-based collection efficiencies do not provide identical measurements. The optical module detects both refractory and non-refractory particles ($d_p > 250$ nm) while the mass-based measurement detects only the non-refractory material within ambient particles (30–;1000nm dva.

As stated, the authors arrive at a count vs. mass based collection efficiency that is the same (0.5), yet, as stated, these do not provide identical measurements; can the

authors elaborate on how (or if) this finding impacts the standard CE used in ambient studies for ensemble mass measurements?

Response: The reviewer correctly notes the lack of clarity in our description of the comparison between single particle count-based and ensemble mass-based collection efficiencies. We have added a new section 3.3 to the manuscript that deals with a comparison between LSSP and MS mode data which are used to obtain count-based and mass-based measurements respectively.

Comment E-1: p. 21331: Figure 3a and 3b exhibit significant scatter that is attributed to uncertainty in the measurements of chemical ion signal, d_{va} and d_o . The standard deviations determined from the binned data are approximately 43%. From which binned data? Using both figures? The standard deviations for the data in 3b are huge.

Response: This information was not provided in the original manuscript. We have re-organized the revised manuscript to include an appendix (Appendix B) that discusses the uncertainties inherent in Figures 4a and 4b (Figures 3a and 3b in the ACPD manuscript).

Comment E-2: p. 21331. "Uncertainty in the chemical ion measurement was determined by analyzing the single particle response of the instrument to known size ammonium nitrate and di-octyl sebacate particles. In laboratory calibration experiments, the variance in single particle ion signal (sum of nitrate ions and organic ions for each particle) for the two different particle types was found to be +/-10%." What does this +/-10% for pure lab generated particles have to do with ambient measurements of real particles given the results shown in this paper? These two types represent a best case scenario for the AMS in that the particles are non-refractive and spherical and thus will undergo prompt and complete vaporization. The key question that this paper brings up is what happens to the AMS standard deviation and quantitative mass concentrations when you include the 77% of the particle mass you are not detecting in prompt vaporization due to bounce or incomplete vaporization of refractory particles?

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



Response: We agree with the reviewer; the variability in the ion signals obtained from ambient aerosol particles of unknown shape and composition will be greater than the variability observed for pure component laboratory particles such as NH_4NO_3 and DOS. But, the particle to particle ion signal variability observed for monodisperse pure component particles provides an estimate, probably a lower bound, for the variability of ion signals obtained from ambient aerosol particles. The second issue raised by the reviewer returns to the topic of how the single particle results impact the non-refractory mass concentration measurements reported by the AMS. As stated before, section 3.3. provides a summary of the connection between the LSSP data and ensemble mode data and details some of the insights that the LSSP measurements provide about AMS mass concentrations obtained from the pToF and MS mode data.

Comment E-3: p. 21331. "The signal-to-noise from the single particle chemical ion signals made during the MILAGRO study were further limited by rather high chamber background signals during the field deployment (single particle chemical ion signals are difference measurements)." The S/N was even further limited beyond the 10% of the lab studies due to other (i.e. non-spherical and/or large) particle types being present.

Response: We agree with the reviewer and we have added the following sentences to the text:

The ammonium nitrate and DOS particles represent a best-case scenario (tightly focused particle beam and prompt vaporization) for chemical detection within the AMS. The variability in ion signal measured for non-spherical, chemically complex ambient aerosol particles will likely be greater than $\leq 10\%$.

Comment E2-1: on p. 21332: This technique identifies inorganic species (ammonium, nitrate, sulfate, and chlorides) and separates their mass spectral signals from particulate organic signals - Since the AMS technique can only detect the mass of non-refractory species, it is mainly sensitive to ammonium nitrate and chloride. It cannot detect most of the signal from other refractory forms of chloride, nitrate, and sul-

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fate such as NaCl, NaNO₃, CaNO₃, KCl, K₂SO₄, and metal chlorides. In fact, these species will most likely produce the delayed and null ion signals that are not used for most of the analysis presented in this paper. Only including the easily detectable particles seriously skews the analysis and thus it is not surprising that many of the particles appear to be composed of mostly ammonium nitrate and chloride, as detailed below. The fact you have limited the analysis to 23% of the particles should be mentioned (again) up front, as a reminder, in the discussion in Section 4.

Response: We have altered the statement about inorganics to say nonrefractory inorganic species in the revised manuscript. We have also included an additional discussion of the potential biases introduced by only discussing the chemical composition of the promptly vaporized particles at the beginning of Section 4.

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

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