

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 #1

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Overall

This paper presents the results from a new method to obtain insight into atmospheric aerosols using a light scattering module interfaced to an aerosol mass spectrometer (AMS). Results are presented from the first atmospheric test of the instrument in Mexico City. The paper is quite interesting and informative. However, there are a number of questions and concerns, as delineated below, that must be addressed before this paper can be published in ACP.

One of the most interesting aspects of the paper is the discussion of the new light scattering module and how it can be used to determine the fraction of particles that

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form a detectable mass spectral ion signal in the AMS using the light scattering signal as a trigger for their presence. The authors use this light scattering signal to determine that only 23% of the ambient submicron particles in Mexico City produce a rapid (useable) vaporization signal. In spite of this finding, the authors then go on to use the signals from this minor fraction of particles to draw major conclusions about all ambient aerosols in the Mexico City atmosphere. The problem with this is the AMS is in fact biased towards the 23% of particles that are detected. In particular, Figure 2 shows the particles with prompt ion signals the AMS detects are biased towards the very smallest particles which represent less than 2% of the total particle counts (and an even smaller fraction of the total mass). Given the well documented size-composition dependence for atmospheric aerosols in the literature and the fact Figure 2 shows the analysis is slanted towards the very smallest particles, there is no question the AMS results as presented are skewed significantly. This finding has significant ramifications for the AMS quantification results both in the current as well as previous and future studies. Importantly, this finding may in fact explain why the AMS sees so much oxidized organic aerosol (OOA or SOA) in the atmosphere—these spherical particles would be selectively detected with close to 100% efficiency since they are the most aged and hygroscopic (i.e. liquid) particles. Primary organics present on fresher less spherical drier particles could be missed due to bounce issues. Thus, the question that should be addressed in this paper is what ramifications does the light scattering finding have on quantification results by the AMS which have always assumed a uniform detection efficiency for all particles? Also, any conclusions that are drawn in Section 4 about the ambient aerosol are questionable at best as far as how representative the particles are of the ambient atmosphere. Section 4 is the weakest part of the paper and perhaps since the paper is so long, it could be removed given the fact it is based on such a small subset of particles.

Finally, there are many places in this paper where the authors digress and compare their measurements and capabilities with single particle mass spectrometers; it seriously detracts from the paper. The two types of instruments were not even at the same

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location for this study. The position the authors take in the comparison is extremely biased and should be removed until a direct comparison can be made.

General questions

There are several other major problems with the manuscript that must be fixed before this reviewer can recommend publication.

The abstract has many claims which are not strongly supported in the paper. It is too long and unfocused (similar to the paper) and needs to be cut back and re-packaged to only claim the things that are actually demonstrated in the paper.

At the beginning, the paper describes the new method for light scattering. However it doesn't mention or cite any other groups that have performed single particle light scattering coupled with chemistry information. These are relevant to the general discussion of this new instrument in the context of previously existing instrumentation striving to obtain similar information. (Murphy, 2004; Moffet, 2005; Moffet, 2008)

Other points:

There are several other major problems with the manuscript that must be fixed before this reviewer can recommend publication.

A) 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. Absorption of 2 photons at 193 nm makes it difficult to detect molecular ions of organics. However, two photons at 266 nm (9.6 eV) corresponds to far less energy deposited in a molecule than the 70 eV used for EI in

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the AMS. Importantly, 2-photon absorption of 266 nm light is just above the ionization potential of most organic molecules and thus far less energy remains in the absorbing molecules leading to far less fragmentation. Using 266 nm for laser desorption and ionization, molecular ions of organic species (i.e. aromatics, acids, levoglucosan and other sugars, methoxy-phenols, PAH, amines) as well as classes of organics (oxidized organics, oligomers, aromatic fragment ions) are frequently detected as discussed in a number of published papers. Also, since atmospheric aerosols undergo a MALDI process, many times intact organics are solely detected as the protonated molecular ion (MH⁺). Ions in the 300 m/z range are often detected in single particle mass spectrometers. In contrast, most ambient AMS organic spectra show rapid decline of ion signal above 50-75 m/z units due to ion fragmentation in the EI source.

Many publications describe the use of other wavelengths such as VUV ionization that yield fragment-free single particle mass spectra for organics. Some of the relevant references are included at the end of this review.

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.

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, 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 sin-

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gle particle mass spectrometers can be found using a relatively quick literature search on Web of Science. Because of the bias shown in the AMS analysis, some could claim single particle techniques may in fact be more quantitative than the AMS which detects a limited subset of the ambient aerosol based on size (very small as shown in Fig. 2) and chemistry (non-refractory compounds only). Also, this new AMS approach is limited for number concentration measurements. The counting statistics are poor but this point is not really discussed in the paper. As shown in Table 1, their major conclusions are based on the chemistry of 2956 particles analyzed over 75 hours. This corresponds to ~ 0.6 particles every minute. In contrast, single particle mass spectrometers have been shown to analyze 300-600 particles per minute. If they choose to keep it, the authors should balance their AMS vs. SPMS comparison by mentioning this drawback for the AMS and elaborate on why the analysis rate is so slow.

C) 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. Quinn et al (JGR, 2008) 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. 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

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aerosol as well as the quantitative potential for the AMS.

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, particle are detected. Figure 2 would be more informative if the x-axis showed particle size instead of time of flight.

D) “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? The other way this statement could be interpreted as written is that the authors are claiming they are detecting 59% of the total aerosol mass in the atmosphere. It is important to clearly explain how this 23% of the particles contained 59% of the mass based on the AMS analysis only.

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.

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This comparison is critical before you can claim the AMS is getting quantitative results. The key question is: how do the authors know how much aerosol mass the other 77% of the particles contained when the ion signals were missing or limited at the least? In other words, one cannot state with certainty how much of the total aerosol mass these particles represented since the AMS cannot measure their chemistry directly.

An important question relevant to the atmospheric chemistry community is how do the findings in this paper impact ensemble AMS mass calculations and quantification? 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? What is the range of values for the CE, as determined using the light scattering signals, over the course of the study?

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 scattering 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.

"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. For many particles (51%), the AMS is not detecting any mass at all.

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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 ($30 < d_p < 1000$ nm 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?

E) p. 21331: Figure 3a and 3b exhibit significant scatter that is attributed to uncertainty in the measurements of chemical ion signal, dva and do. 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.

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 $\pm 10\%$."

What does this $\pm 10\%$ 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?

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.

E) 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 sulfate 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.

p. 21332. "For the range of refractive indices expected in the MCMA (real refractive indices of 1.4–1.6, Seinfeld and Pandis, 2006), the uncertainty in do is $\pm 10\%$ (Cross et al., 2007)."

It isn't clear why the authors have to estimate these values when they have been measured in the MCMA area. It would be much more appropriate to use the measured

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refractive index values reported in Moffet et al. (JGR, 2008) for Milagro. The reported range is significantly larger than this which would lead to a larger uncertainty in D_0 .

F) p. 21335: This agreement is shown quantitatively in Fig. 6b which displays the correlation between the LSSP and PTOF signals for arrival times between 3.1–5.5 ms (data between arrows in Fig. 6a). The correlation is linear with a slope of 0.85, indicating that the LSSP mode collected 85% of the PTOF signal. We note from Fig. 6a and 6b that the LSSP signal is about 15% smaller than the than the signal obtained in the PTOF mode. The missing 15% is likely due to delayed vaporization of particles smaller than the optical size detection limit and therefore are not detected in the LSSP mode. This interpretation is further supported by the fact that at longer times-of-flight (>4.8 ms in Fig. 6a), the average LSSP and PTOF modes agree fully.

The statements regarding Figure 6 are quite confusing. There needs to be a better bridge between Figures 2 and 3 which shows a minor fraction of the smallest particles were detected and Figure 6 which is used to state that the LSSP mode collected 85% of the PTOF signal. There is a serious inconsistency in these results as they are explained.

G) p. 21336: The observation of two distinct particle types within the same chopper cycle indicates that the ambient ensemble was externally mixed during this sampling period.

Are the authors actually stating that two particles are used to determine the entire ambient ensemble was externally mixed? Out of how many? Statistically, this is a weak statement based on only 2 particles. How do the authors know these 2 particles were representative of the entire atmospheric aerosol?

H) p. 21336: They use 3 different methods to calculate mass. Depending on which method is used, they get a range of sizes ranging from 211 to 446 nm for the same particle. Which method is most trustworthy and has the least error and required as-

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sumptions? This is a wide range for mass estimates and seriously calls to question the ability to be "quantitative". If this is the error for 1 particle, then it will be multiplicative for many particles.

I) p. 21337: The mass of particles 1 and 2, as measured by the calibrated mass spectrometer, is 18.2 fg, and 13.0 fg, respectively.

How is the mass spectrometer calibrated for this experiment—using ammonium nitrate? If so, how will this affect the absolute magnitude of the mass of each particle if they contain completely different components with different densities (and shapes)?

Also, should read "masses" and "are" 18.2 fg…

I) p. 21338: “The simultaneous observation of these two externally mixed particles illustrates the capabilities of the LS-ToF-AMS technique to provide a measure of the mixing state and atmospheric processing of ambient submicron aerosol particles.”

This is an over-statement and should be removed. Showing the data for two particles is not really demonstrating the full potential of the technique. Higher statistics than just 2 particles would be far more appropriate.

J) p. 21338: “A unique feature of the LS-ToF-AMS is that it provides ensemble as well as single particle measurements.”

Unique compared to which other method? This statement is true for any single particle method—one can always get an average from multiple particles, and in fact can do so on a selective basis. However, it is true that one cannot go in the reverse direction (i.e. from an ensemble to single particle data).

K) p. 21341: “In order to limit any potential effects of particle bounce, prior to full vaporization of the non-refractory component of single particles, we have chosen to analyze only the prompt vaporization single particle events (refer to Sect. 3.1). Comparing the single particle mass measured by chemical ion signals with the mass

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derived from dva and do measurements indicates that approximately 88% of the single particle mass is accounted for by the chemical ion signals (Fig. 3a). The remaining ~12% may be due to refractory material (dust, metals, black carbon, etc.) that the AMS does not measure.”

This is a critical point in the paper that could be lost on the general reader. So, for clarification, for all analyses from this point until the end of the paper (i.e. all of Section 4), are you using only 23% of the particles to draw conclusions about the entire ambient aerosol? It is unclear how the conclusions are realistic for such a limited subset of particles. One of the conclusions is the reported measurements are accounting for 88% of the single particle mass. There is a serious disconnect here. As stated, the AMS analysis excludes non-spherical and refractory particles. It excludes most of the larger more massive particles, as well. They have stated they are analyzing 23% of the signal and thus not using 77% of the mass—yet they claim they are only missing 12%. This is a discrepancy that needs to be addressed.

Also, the authors need to be clear throughout the rest of the paper when making broad generalizations about the ambient aerosols from which they are drawing their conclusions. The reader is left pondering what the other 77% of the non-detected aerosols were composed of. Since the paper is very long, the authors may want to think about eliminating Section 4 since it is the weakest part of the paper.

L) p. 21341: “Typically, dust and soil particles fall into the super-micron size range, which is not detected with the AMS due to transmission efficiency losses for larger particles (Lui et al., 2007).”

Should be noted, the AMS also doesn't detect any size of dust (salts) because they are refractory and thus not volatilized at 600 degrees. Industrial dust/salts were detected down into the submicron size range.

M) p. 21342: “Levoglucosan (1,6-anhydro-_-D-glucopyranose), the pyrolysis product of cellulose, is a well-established marker for the combustion of biomass mate-

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rials (Simoneit, 2002). Once partitioned into the particle phase, levoglucosan does not degrade, making it a useful tracer for long-range transport of biomass burning aerosol (Fraser and Lakshmanan, 2000).”

There are many other more recent papers in the literature which call into question the use of levoglucosan as a robust tracer of biomass burning. The authors need to give a balanced (and up to date) perspective—different fuels, aging processes, etc. are shown to change the relative amount of levoglucosan in biomass burning aerosols. Others have shown levoglocosan decreases in intensity in aged biomass burning aerosols detected with the AMS (Coe, JGR, 2008). The Carnegie Mellon group has also shown levoglucosan decays away in recently conducted chamber experiments. So, it is highly likely this 5% is a serious under-estimate and missed fresher (less spherical) or larger (more aged) biomass burning aerosols. The amount was also smaller during this period as the region had many rain events, as pointed out in the paper. Finally as shown recently by electron microscopy results, the majority of the Mexico City particles contained potassium and were non-spherical biomass particles…due to shape issues, would most of these irregularly shaped biomass/biofuel particles bounce and not be detected like ammonium sulfate?

Thus it is questionable with all of these caveats to make any major claims as to an estimate of BBOA at T1 for the study…Yet, at the bottom of p. 21342, they state:

"While the absolute magnitude of biomass burning sources may not be adequately represented in the current data set, our single particle measurements indicate that biomass burning was a relatively minor source for particulate matter at T1 during the sampling period under discussion."

N) p. 21343: They state: “With these particles removed, the reconstructed organic (HOA+OOA) accounted for 93% ($R^2=0.84$) of the measured single particle organic mass, suggesting that HOA and OOA give a reasonable, but not complete, description of the organics at T1.”

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Again, this general conclusion is based only on the 23% of the particles producing prompt ion signals? This needs to be clarified.

O) p. 21344, they state: "Based on this observation and on mass balance, we will assume that the inorganics were in the form of NH_4NO_3 , $(\text{NH}_4)_2\text{SO}_4$, and NH_4Cl ;"

These are the forms of nitrate, chloride, and sulfate the AMS can detect. The other forms such as NaNO_3 , NaCl , KCl , metal-chlorides and metal nitrates may not be detectable in the AMS. The vaporization temps of the Na and K inorganic salts are above 800 degrees and thus these are refractory species in the AMS.

P) p. 21344: They state: "The single particle data directly confirm assumptions that are typically drawn from ambient, ensemble sampling of size-resolved aerosol chemistry where the average chemical compositions of particles appear to be relatively constant as a function of particle size (Salcedo et al., 2006)."

This is a strong statement and not really appropriate considering they are analyzing a narrow size range at the smallest sizes of the total aerosol as shown in Figure 2. The MILAGRO paper by Moffet et al. cited throughout this paper shows a very strong size dependence on chemical mixing state in Mexico City. Also, as the particles grow in size, they show more signs of aging. External mixtures are far more prevalent at the smallest sizes (and above 1 microns). These may be out of the size range of the AMS used in this study—and thus an ensemble average may be representative of the very narrow (small) size range the AMS seems to be detecting with prompt vaporization signals. In other words, this is more of a conclusion regarding the specific aerosol the AMS can efficiently detect versus the aerosol that is actually present in the atmosphere.

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

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