

The authors thank Referee #2 for their useful comments. Replies and further commentary in response to the referee's comments, including modifications to the submission, are presented below.

1)

- a. **The signal response vs. particulate mass sampled should be a linear function. While the data points generally fall upon the dashed line, the points measured at higher mass loadings (40-100 pg) show significant deviation. One would expect less scatter at higher loadings due to better signal-to-noise ratios. In fact the data look like they might be better fit to a non-linear function. The authors need to address why this might be so.**

In retrospect, the plot in Figure 2 may be misleading. The black squares represent individual measurements (i.e., sampled particle mass followed by AMS analysis). Note that the exact mass sampled is calculated from the total aerosol mass (C_{OA}) of oleic acid measured with the SMPS and knowledge of the sampling rate (through the aerodynamic lens) and sampling time. Therefore, each point in a "grouping" represents a slightly different mass. The red triangles were added as averages for "reasonable" groupings of signals from similar mass depositions. The triangle at the highest average takes into account only the two highest sampled masses, which, misleadingly, appears to show a greater error. We do not believe that this scatter is due to shot-to-shot fluctuations in the near IR laser. Typically, the instrumental variability (shot-to-shot) is about 10%.

To avoid confusion, the averaged points have been removed from the response curve.

As to the linearity of the response, we agree that the response at higher sampled masses appears to roll over; however, we hesitate to make that statement based on only the few measurements at higher mass. As the AI wire probe is prone to fouling at these higher sampled masses, we did not take many measurements on the high end of the response curve. As a result of our electronic data processing we can see signal saturations under conditions of large sampled masses (this is discussed in more detail in the "Responses to comments by Referee #1" document available online). However this is a function of the instrument sampling time which can be varied accordingly. Our focus in this work was extension of the analytical capabilities of aerosol mass spectrometers to low mass loadings and as such, the measurements below about 40 pg deposited are of greatest interest. Clearly we cannot make a substantive statement about the linear dynamic range based on this data set.

- b. **Measurements at higher mass loadings, while not atmospherically relevant, do provide critical tests of the method to determine over what range this instrument operates linearly. For example, do the authors see saturations effects at high loadings? Are there space charge limitations that ultimately determine the linearity of the signal with loading? At higher loadings how do the authors know that all of the aerosol is completely desorbed and ionized from the AI probe?**

It should be emphasized (and is stated in text in the beginning of subsection 3.1) that Figure 2 represents all low-loading chamber conditions (0.15 to 4.4 $\mu\text{g m}^{-3}$) for oleic acid. The particles were collected for variable times (5-30 s, as stated) to achieve the particulate mass range sampled. Thus, "higher loadings" may more accurately be termed "more particulate mass sampled". As mentioned above signal saturation is observed for very high mass samplings due

to data processing limitations; however the mass sampled onto the probe is also a function of deposition time and it is important to differentiate between higher particulate concentrations which is a function of the aerosol analyzed and mass sampled which can be adjusted for instrumentally.

We confirm that all of the particulate mass is desorbed from the probe by firing the NIR laser until no ion signals are observed. Typically this requires 1-2 laser shots for low masses sampled to 10-20 at the high end. In all cases, once data acquisition is completed, the laser is fired at 20 Hz for 1 minute to ensure that any residual collected sample has been removed from the probe.

While it is possible that space charging effects are affecting ion signals at higher sampled masses, no systematic studies were conducted to support such a hypothesis. We do believe that if space charging were significant, then likely it would result in degradation of the mass spectral resolution, which is not observed.

- 2) It is difficult for a reader to draw any firm conclusions from Fig. 4 regarding the time evolution of the chemical constituents of the alpha pinene SOA. This is in part due to the figure format itself. The authors should recast this data as a two dimensional plot (Ion Intensities of various peaks vs. Coa) so the reader can more closely compare individual ion species with the total aerosol loading (i.e. Figure 3a) for example. The authors then need provide a more detailed discussion of the time behavior of the various aerosol components. Do most of the ion signals simple grow with Coa or do various components evolve in different ways as the aerosol is formed? Do the authors see changes in partitioning as a function of loading?**

The intent of Figure 4 was to demonstrate the capacity of NIR-LDI-AMS to monitor product ion evolution as a function of time and/or C_{OA} . Nonetheless, we agree with the reviewer that a 2D plot would clarify the discussion and, in line with the Referee's suggestion, we have added such a 2D plot (and associated discussion) showing temporally different behavior of two product ions.

Alpha-pinene was selected as a model SOA system because it is well studied. The intent of this report was not to elucidate the oxidative chemistry of this terpene or to discover new chemistry. Therefore, we do not believe that a more detailed discussion of the temporal behavior of these key aerosol components is within the scope of this technical report.

- 3) The mass spectra (figure 3) of the alpha pinene SOA contains only a handful of peaks (5 or so assigned) between m/z 100-300, which suggests that the SOA formed is rather simple chemically. While the authors do a good job of putting the peaks they do assign in the proper literature context, this mass spectrum is significantly less congested (with fewer high molecular weight features) than others reported in the literature using a variety of ionization sources (e.g. VUV, APCI, etc.). This deserves more discussion than what is currently included in the manuscript.**

One of the key points of this submission was introducing a new online AMS method that would be of utility for chamber experiments employing atmospherically relevant concentrations of SOA, which has been called for in several recent comprehensive reviews on SOA (Kroll and Seinfeld, 2008; Hallquist et al., 2009). As we will more strongly emphasize in the resubmission, we chose to demonstrate the utility of NIR-LDI-AMS for these SOA studies by employing SOA

derived from the ozonolysis of α -pinene since this type of SOA has been the most widely studied biogenic SOA to date (see numerous references in the aforementioned reviews).

We agree with the referee that our current presentation may make the SOA derived from the ozonolysis of α -pinene appear more chemically simple than reported by others, which was not our intention. We chose to focus on assigning well-known products, including pinic and pinonic acid, again, mainly as proof-of-principle of the NIR-LDI-AMS method. We did not intend, nor do we intend, to demonstrate “new chemistry” for SOA derived from the ozonolysis of α -pinene in our *preliminary* report on a novel methodology: rather our intention was to show the instrumental capacity of NIR-LDI AMS to determine composition of SOA particles at low mass loading that will be applied to chemically meaningful questions about SOA in upcoming reports.

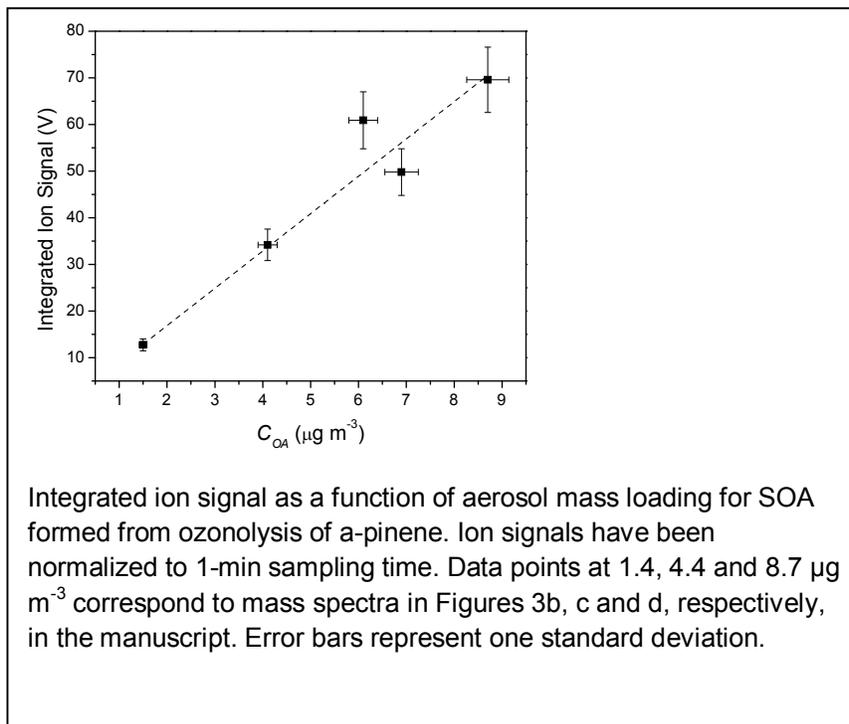
An additional statement will be added to the revised manuscript clearly stating to the reader that this is only a brief analysis of the more prominent ion signals as an example of the utility of the NIR-LDI-AMS technique and referring to the literature for more comprehensive chemical discussions.

It should also be noted that we scaled the mass spectra to the height of base peak, which was 185 m/z in all the reported (and recorded) mass spectra for this system. There is clearly HMW product formation, including oligomers, which coincide with higher C_{OA} levels and longer reaction time, with m/z upwards to 300. These ion signals, which comprise only a small portion of the total ion signal at these low values of C_{OA} , are clearly visible with the appropriate rescaling of the mass spectra.

An inset will be added to Figure 3d to clearly show the ion signals at higher m/z.

- 4) The authors need to estimate what fraction of the total SOA they are detecting so the reader can get a sense of how quantitative the technique is for measuring SOA. I would like to see a plot of the total ion signal as a function of SOA loading or reaction time. Does the total ion signal follow the total aerosol loading? A plot of total ion signal vs. aerosol loading could be compared to Figure 2 to better elucidate whether the instrument response is similar to that of a pure particles (Oleic acid).**

By integrating the total ion signal in the mass spectra (see Figure below), it is clear that the ion signal does follow aerosol mass loading (and mass sampled as was shown for the POA oleic



acid); however, at this point it is not possible to estimate what fraction of the total SOA is being detected. Such a measurement, while significant, would require measurement response factors for each compound or a general response factor for compound classes, neither of which is readily possible for such complex and variant chemical systems as are encountered in even the simplest SOA forming processes. Such an undertaking, even if it could be performed successfully for each chemical system of interest, is beyond the scope of this present report.

References

Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, T. F., Monod, A., Prévôt, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, *Atmos. Chem. Phys.*, 9, 5155-5236, 2009.

Kroll, J. H., and Seinfeld, J. H.: Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere, *Atmos. Environ.*, 42, 3593-3624, 2008.