

Interactive comment on “Collection efficiency of α -pinene secondary organic aerosol particles explored via light scattering single particle aerosol mass spectrometry” by Ellis Shipley Robinson et al.

Anonymous Referee #2

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Review of Robinson et al

The paper by Robinson et al. presents a study of AMS collection efficiency for laboratory SOA from the commonly studied α -pinene + O₃ system. It uses two techniques to quantify CE, the light scattering single particle mode of the AMS (LSSP, yielding CE_p) and a comparison to an SMPS (CE_m). It goes into an unusual level of detail in describing the results, and will represent a very useful addition to the AMS literature. I support publication in AMT, after the issues listed below are addressed.

Major issues

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(1) A key problem is that the manuscript, as currently written, will be very confusing for most AMS users. The wording is quite specific and a clear connection to the way most users utilize the AMS is not given anywhere. My estimate is that 99% of published AMS figures use MS-mode data only, ~1% use PToF mode, and ~0.1% or less use LSSP mode. This may become even more skewed towards MS-mode data in the future as the number of ACSMs (that only have MS mode) surpasses and then greatly exceeds the number of AMSs in use. Thus it seems critical to clarify the implications explicitly. This could be done with a section such as “Implications for AMS and ACSM” users before the conclusions, or maybe a paragraph in the conclusions.

In particular the fact that some particles do not evaporate within the PToF timescale or don't give LSSP signals is of no direct relevance to users of MS mode data in terms of data processing etc. (even if they are still useful for users wishing for a deeper understanding of the instrument, but which lately are few and far between). Only the fractions that are not detected using MS mode (i.e. CE_m) are relevant to the vast majority of AMS/ACSM practitioners.

As an example of this issue, in P8 L259-261 the wording is quite confusing. 5 s is not an arbitrary long timescale. It is the timescale of the MS mode of the AMS, from which mass concentrations are always reported. This should be clarified.

(2) There is a small fraction of the signal for non-refractory species that is detected over even longer timescales than the MS mode open / closed alternation, and thus contributes to slower variations in the AMS background signals (“MS closed”), as documented in e.g. Huffman et al. (ACP 2009, cited in the manuscript). For semi-refractory species, such very slow signals can be larger and even dominant, but even then they can be used to extract particle concentrations (see e.g. Salcedo et al. 2010).

Did the authors examine the variations in the background of the mass spectrometer (MS closed) during their experiments? It most likely contains information that is very relevant to this paper, in particular signals from the evaporation of bounced particles.

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This should be analyzed and discussed in the revised paper.

(3) An important limitation of the results of this study is that the SOA was formed at extremely high concentrations (1500 ug/m³). Those concentrations are not atmospherically-relevant, and the composition of the SOA formed cannot be expected to be the same as for much lower, atmospherically-relevant concentrations. For example typical concentrations at Hyytiälä, Finland (a location where α -pinene SOA is important) are ~ 1 ug/m³, a factor of 1000 smaller than in this study. Shilling et al. (2009) showed that the composition of α -pinene + O₃ SOA changed very strongly between 0.5 and 140 ug m⁻³, with very large changes below 30 ug m⁻³. The results of this study, while important in terms of characterizing the AMS detection system, should not be recommended for application for ambient particles in terpene-dominated environments. The fact that the SOA was generated at very high concentrations, and thus that it is not clear whether the results will be applicable to ambient SOA from this precursor and oxidant, needs to be stated prominently in the abstract and conclusions of the paper.

(4) The need to use extremely high concentrations would appear to be a critical limitation of this technique. It is important that the author discuss what the lowest concentrations that could possibly be studied with the LSSP method are, as well as possible methods to allow performing similar experiments at lower SOA concentrations. Did the authors try to use small seeds? E.g. using 10 nm seeds from (for example) an electrospray aerosol source), that would then be coated by a much larger amount of SOA. Presumably the CE would be dominated by the SOA coating, and insensitive to the initial seed. The authors are creative experimentalists and may have better suggestions, and it would be useful to document those in the paper.

(5) Fig. 5 and P9 L271. Apparently a very short chopper time (5 ms) was used for these experiments. This is unfortunate, as the AMS can typically be operated at >10 ms, which would have provided better data. Similarly the mass spec. pulsing frequency was too long (30 μ s), and a shorter frequency would have allowed recording single particle

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events in more detail. Both items should be recommended in this paper to future experimenters wishing to use this technique, so that improved data can be acquired.

(6) P10, L301-307. I would argue that this is an extremely important point. I.e. the confusion of many users about the potential variability in CE, and the large effort needed to estimate it accurately, has obscured any trends in RIE that might be present on the laboratory and field data. Methods such as in the current paper where CE is quantified allow investigating RIE, which is a timely topic. It seems to me that this should be mentioned more prominently, e.g. in the abstract and conclusions.

(7) P11, L336-342. An alternative hypothesis (that appears much more likely than the 2 mentioned here) is that a particle bounces from the vaporizer without any evaporation, and then lands into a colder surface in the ionizer. The AMS ionizer cage is heated to ~ 250 C by the electron emission filament, and thus NO prompt evaporation at all should be expected for most species when impacting that surface. Given the geometry of the AMS ionizer, most bounced particles will impact the AMS ionizer cage. If they exit the cage region, they will end up on surfaces which are much farther and much colder (~ 30 C). This hypothesis can explain why substantial more particle mass is detected in MS mode than in PToF mode, as the colder temperatures (~ 250 C) result in far slower evaporation. Can the authors incorporate this hypothesis into their discussion, even if these particles may not be detected at all in PToF mode?

(8) P11, L344, this result can be influenced by "threshold bias". I.e. some particles may start to evaporate more slowly per the previous comment, but not be detected at all in by the ion threshold used in single particle mode. This appears obvious from the distribution of signals of the delayed particles in Fig. 5, which would have kept increasing in frequency towards lower signals than the threshold used here.

Maybe only those particles that impact the ion cage very close to the filaments, in an area that is likely much hotter than 250C, may lead to the sharp delayed particles.

Overall while this discussion is valuable, it is incomplete. A physical schematic (car-

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toon) of the different possibilities for particle trajectories and associated signals would be useful for readers of the papers and for future discussions (e.g. at AMS Users Meetings and in future papers). This should include particles completely missed due to threshold bias under slow evaporation. I strongly encourage the authors to add it here, and include the additional possibilities mentioned in the previous paragraphs (even if the present data do not allow characterizing all of them). Similarly, on P11, L375: this hypothesis is not proven with the current data, since other particles may have been completely missed due to threshold bias.

(9) P12, L388, and L395-397. This text and axis label should be “upper limit of distance bounced” as particles will lose energy and reduce their speed upon collision. The conclusion on L397 about many bounces being common is not really supported. E.g. if the particles lose 90% of their speed upon the first impact, then they may just evaporate on the 2nd impact, with a distance that the authors would calculate as 10 cm, but would only really be 1 cm. There is some data on velocity changes upon impact for much larger particles (e.g. Li et al., 1999). I did not find results for submicron particles on a quick search, but they are probably out there. One would expect that submicron particles will lose a much larger fraction of their speed, due to the far larger ratio of adhesion forces to inertia, compared to the data in Li et al. The authors should do a more thorough search and use the results to inform this discussion.

(10) P12 L401-402: this conclusion could be made if adhesion/adsorption forces did not change between the two temperatures. But for example Fig. 11 of Hu et al. (2016) shows that chloride detection in the standard vaporizer becomes slower when going from 600 to 835 C. This effect is not observed for other species, indicating that it depends on the specific chemistry of the system being studied. This seems to be the case here as well, see next comment. So I don't think that the conclusion about where this tail comes from is as obvious as the authors state. Note that the ionizer surfaces will be somewhat hotter with a hotter vaporizer, due to radiation heat transfer which is efficient at those temperatures.

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(11) P12 L403-405. This statement is incorrect. It is clear from the data in Fig. 9a (of this paper) that SOA detection has a LONGER tail at 800C. Although the signal is noisy, a fit or smoothing of the data (as I did just by eye) clearly reveals this feature. Also only the front baseline region should be used to provide a zero level for the data (“DC marker region”), which will also increase the difference. At present the average of the front region is clearly negative.

(12) P12 L404-406, here it is unclear whether the signal plotted in Fig 9c is exclusive to α -pinene SOA. If the m/z 43 signal arises from both squalane and SOA (as expected from the NIST spectrum of squalene <http://webbook.nist.gov/cgi/inchi?ID=C111013&Mask=200#Mass-Spec>, and noting that the AMS spectrum will have substantially higher m/z 43 than the NIST one), it is possible that the signal shown in this figure is dominated by squalane, and thus that the conclusion reached here is incorrect. The authors have experience identifying signals dominated by one or another species/sources in binary mixtures, and that method should be applied to improve this graph and hopefully clarify whether the conclusion is correct.

(13) P13 L 409-420. This conclusion can only be made if the arrival times (initial onset of the signal) are shown for NH_4NO_3 , which is not currently done. Fig 9b seems to show a secondary mode that could be due to delayed particles. The author should investigate and document this.

(14) P13 L 434-436 and Fig 10: the NH_4^+ fragment is shown for ammonium sulfate. This is typically not detected in AMS spectra (e.g. Table 1 of Hu et al., 2016, which is derived from high-resolution data). Presumably the authors are analyzing unit-resolution data and mislabeled the ion. This fragment is almost certainly H_2SO_4^+ , a major ion observed for $(\text{NH}_4)_2\text{SO}_4$. More H_2O is expected to arise from the decomposition of H_2SO_4 , a process more important for the prompt particles, as Fig. 10b shows. It is important to fix this as it could otherwise cause a lot of confusion in the AMS community. (Alternatively, if the authors had high-resolution evidence of NH_4^+

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detection at such a large fraction as shown in the figure, it would be big news).

(15) P14 L 466-467: How can LSSP separate prompt and delayed particles of different sizes, when sampling a polydisperse aerosol? It seems (from e.g. Fig. 4) that this would be extremely difficult, unless all particles were prompt, which is not the case here. This is important since the polydisperse data in the blue experiment seem to show an increase with size, while the (much more trustable, in my opinion) monodisperse data do not.

(16) P2 L35: Jimenez et al does not state that RIE_{org} is assumed to be the same for all organic species. It does actually provide some cross-section data that could allow grouping hydrocarbons and oxygenates separately. The assumption of the same RIE_{org} for all organics in the field was introduced later based on experimental results at Aerodyne, and to my knowledge Canagaratna et al. (Mass Spec. Rev. 2007) may be the first publication of that assumption. To my knowledge it has never been published that all organics in the lab should be analyzed with RIE = 1.4, rather than calibrated for each experiment (especially given wide variability in CE of organics, as documented by e.g. Bahreini et al. (2005) and Docherty et al. (2013). Although that has been a common misinterpretation. See Jimenez et al. (2016) for further discussion of this topic.

(17) P16 L522-524. Returning to issue #1 and the implications for most AMS/ACSM users. I would argue that for the vast majority of AMS users, CE IS a serious limitation. While the information obtained is undoubtedly of high interest, very few AMS groups have the technical skill, equipment, and time to perform and interpret analyses such as the ones in this paper (as evidenced by the very few publications on CE using LSSP). In my opinion the adoption of the capture vaporizer that may lead to CE~1 for ambient particles (Xu et al., 2016; Hu et al., 2016; and work in preparation that is documented in relevant presentations at AMS users meetings <http://cires1.colorado.edu/jimenez-group/wiki/index.php/AMSUrMtgs>) may be much more useful for the vast majority of AMS (and especially ACSM users). The authors may want to comment on the rela-

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tive advantages and disadvantages of both methods, which is a topic of current high-interest for the AMS community.

Other issues

(18) P2 L36: it is unclear what the end of the sentence about matrix effects means. Has someone shown that there are no matrix effects? If so, reference(s) should be provided. Or is that an assumption? Or do the authors have unpublished data that shows this?

(19) P3 L90: this statement is very incorrect for m/z 57. It is well-known that m/z 57 is only dominated by C₄H₉⁺ for pure HOA-type species, but in SOA its contribution is often smaller than for the main oxygenated ion at that m/z, C₃H₅O⁺. See for example P25 of the Supp. Info. of Aiken et al. (2009), but this has been reported in many studies. Many types of SOA reported by Docherty et al. are very oxidized, and this statement will certainly be incorrect for those.

(20) P6 L178, this is not completely correct. Two particles may arrive so close in particle time-of-flight that they cannot be distinguished from the signal traces. Presumably the probability of this phenomenon is low, and should be quantifiable with the available data. This should be briefly mentioned and quantified.

(21) P7 L225, which AMS size distribution was used for alignment? (LS or MS)

(22) P9, L285, I would add "for ion formation" to "for ion extraction." E.g. a particle may end up in a location where the vapors do not overlap efficiently with the electron beam. In fact I would expect ion formation to be the dominant effect.

(23) P10, L315-319. Related data has recently been published by Hu et al. (2016). In their Fig. 14 these authors report that the lowest temperature at which monodisperse particles of a given species are detected in a narrow size distribution is proportional to the melting and boiling/decomposition temperatures of the species.

(24) P13 L439, I think this should be "thermal decomposition" (of neutrals) rather than

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fragmentation (of ions).

(25) Fig 7, the fact that α -pinene SOA bounces similarly to ammonium sulfate is a useful result that could be highlighted. Even though Bahreini et al. (2005) and Docherty et al. (2013) have reported similar results, this is still lost on many researchers.

(26) P14 L478-479. Perhaps a better explanation is that the particles shrank due to evaporation, and were too small for the LSSP mode? Poulain et al. (2010) (Fig 7) and Huffman et al. (2009) (Fig 4) show that \sim 20-30% of the mass of α -pinene SOA remains detectable by the AMS at 110C (and those numbers are known to be biased low due to the lack of detection of particles smaller than \sim 50 nm by the AMS).

Also, the thermodenuder is not described in the experimental section or here, and no reference is provided. This needs to be documented in the manuscript, including whether the temperature profile was accurately measured and how (which is relevant for the comparisons with other studies), and what the residence time was. The above results are for Aerodyne-style TDs with typical residence times of 15 s at room temperature. If the residence time was much larger in the TD used here, perhaps that could also explain the difference between the studies.

(27) P15, L491-492, wording is confusing and I think incorrect. The SOA from the present study is similar to the least oxidized OF ALL THE SOAs that had CEM \sim 0.2 in Docherty et al. But the text currently refers to the least oxidized SOA in the Docherty study, which had f44/f57 of 0.06 and not 5. The difference of a factor of x2.5 between this and the Docherty study would seem important and could use more discussion.

(28) The abstract mentions substantial variability in CE_p, but does not discuss whether it is random, or whether it is explained by some experimental parameters. Reading the paper it would seem that it would seem that it is mostly experimental variation, but I suggest that this is directly addressed and clarified.

Wording etc.

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(29) P1 L10: "appear within the chopper window" will not be understood by non-AMS practitioners

(30) P2 L40: "the another"

(31) P2 L52, should be "vacuum aerodynamic diameter" as there are other definitions of aerodynamic diameter that apply for other instruments.

(32) P3 L64, 65, 66, "ToF" and "time-of-flight", when used alone, are easy to confuse with the mass spectrometer. For this reason the AMS community uses "PToF" to refer to "particle time-of-flight" and associated chambers, data, software etc. (as opposed to ion time-of-flight).

(33) P4 L99, it would be clear if the denominator read "All particles detected by LS". Otherwise it is ambiguous and potentially confusing.

(34) P4 L123, solution should be plural

(35) P4 L125, presumably the authors mean milliCuries (mCi) and not milliCoulombs as written

(36) P5, L138, "flash vaporization" would not create particles but vapors, unless it is followed by nucleation and condensation of the vapors. A clearer name for the technique may be "evaporation-condensation" or something like that.

(37) P5, footnotes: neither of the web links given in the footnotes work.

(38) P9, L299. Given that PhD theses are harder to obtain and are not peer-reviewed (at least not in the same way as papers), I suggest that this reference is replaced (or supplemented) by the peer-reviewed paper by the same author and year (Alfarra et al., 2004), which contains the same information cited here. This may apply to other instances of the same reference elsewhere in the current paper.

(39) P10, L304, many RIE_{org} values have recently been published (Jimenez et al., 2016).

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(40) Fig 7b, perhaps a log horizontal axis would work better to see the trend to 1 s?

(41) P10 L319, Saleh et al. is not yet published in AS&T. (As an aside, the data mentioned in comment #23 may be relevant to that paper).

(42) P10, L328-330. The notation for CE' and CE is confusing. I recommend using instead M and P superscripts for the MS and PToF modes, respectively

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