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Collection efficiency of α -pinene secondary organic aerosol particles explored via light-scattering single-particle aerosol mass spectrometry

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Abstract. We investigated the collection efficiency and effective ionization efficiency for secondary organic aerosol (SOA) particles made from α -pinene + O₃ using the singleparticle capabilities of the aerosol mass spectrometer (AMS). The mean count-based collection efficiency (CE_p) for SOA across these experiments is 0.30 (± 0.04 SD), ranging from 0.25 to 0.40. The mean mass-based collection efficiency (CE_m) is 0.49 (±0.07 SD). This sub-unit collection efficiency and delayed vaporization is attributable to particle bounce in the vaporization region. Using the coupled optical and chemical detection of the light-scattering single-particle (LSSP) module of the AMS, we provide clear evidence that "delayed vaporization" is somewhat of a misnomer for these particles: SOA particles measured as a part of the AMS mass distribution do not vaporize at a slow rate; rather, they flash-vaporize, albeit often not on the initial impact with the vaporizer but instead upon a subsequent impact with a hot surface in the vaporization region. We also find that the effective ionization efficiency (defined as ions per particle, IPP) decreases with delayed arrival time. CEp is not a function of particle size (for the mobility diameter range investigated, 170-460 nm), but we did see a decrease in CEp with thermodenuder temperature, implying that oxidation state and/or volatility can affect CE_p for SOA. By measuring the mean ions per particle produced for monodisperse particles as a function of signal delay time, we can separately determine CEp and CEm and thus more accurately measure the relative ionization efficiency (compared to ammonium nitrate) of different particle types.

1 Introduction

Organic aerosol (OA) comprises a significant fraction of submicron atmospheric particulate mass, ranging from 20 to 90 % (Kanakidou et al., 2005; Jimenez et al., 2009). OA has been shown to have negative impacts on human health (e.g., Lozano et al., 2013) and remains highly uncertain in its effect on radiative climate forcing (e.g., Solomon et al., 2007). The physical and chemical characteristics of OA can vary dramatically and depend strongly on source, location, atmospheric age, and other factors. Despite the ubiquity and importance of OA, real-time measurements are technically challenging due to the wide range of chemical composition, particle size, and volatility represented by OA in the atmosphere.

The aerosol mass spectrometer (AMS, Aerodyne Research, Inc.) is used widely in both ambient and laboratory measurements of OA. It has enabled significant advances in our understanding of how organic aerosols form (Craven et al., 2012), age (Aiken et al., 2008), and mix (Robinson et al., 2013) by providing real-time measurements of size-resolved composition and mass for submicron, nonrefractory particulate matter (NR-PM₁). However, a lingering challenge with full quantification of NR-PM₁ in the AMS is the mass collection efficiency (CE_m; Canagaratna et al., 2007), which is the ratio of the measured AMS mass signal to the actual NR-PM₁ mass concentration. Another factor influencing calibration of the AMS mass response is the speciesspecific relative ionization efficiency (RIE) of analyte; this is relative to a calibrant, typically ammonium nitrate. However, an average RIE value is often applicable to most organic species (Canagaratna et al., 2007; Jimenez et al., 2016); there can be some variability in RIE for specific organic species. RIE is not believed to be subject to matrix effects.

To obtain quantitative agreement between the AMS and other collocated instruments in field campaigns, CE_m is usually applied to correct for the consistently lower AMS-measured mass. CE_m can be written as

$$CE_m = \frac{S_{AMS}}{S_O},\tag{1}$$

where S_{AMS} is the signal from the AMS and S_O is the signal of another (perfectly calibrated) instrument. Importantly, this calculation assumes ideal operating conditions for both instruments and the application of all other appropriate correction factors. For example, Drewnick et al. (2003), in a sulfate aerosol intercomparison study, applied a scaling factor of 2.41 ($CE_m = 0.42$) to the AMS-measured sulfate to achieve good agreement with a collocated particle-into-liquid sampler (PILS) instrument. In another example, Middlebrook et al. (2012) recently reported parameterizations of CE_m for ambient sulfate-containing particles that could be used to predict CE_m based on particle acidity and mass fraction of ammonium nitrate. High CEm values were consistent with predicted liquid phase state at 298 K. Thus, CE_m should be thought of as a sensitivity factor that varies for particle types with different compositions and phase states.

Huffman et al. (2005) define CE_m as the product of three size-dependent terms:

$$CE_{\rm m}(d_{\rm va}) = E_{\rm L}(d_{\rm va}) \times E_{\rm S}(d_{\rm va}) \times E_{\rm B}(d_{\rm va}), \qquad (2)$$

where $E_L(d_{va})$ is the lens transmission efficiency as a function of vacuum aerodynamic diameter, (d_{va}) ; $E_S(d_{va})$ is the striking efficiency of particles on the AMS vaporizer transmitted through the lens to the time-of-flight chamber; and $E_B(d_{va})$ is the vaporization efficiency of particles that strike the vaporizer surface, also known as "bounce" because particles can bounce away from the vaporizer surface and escape detection. Any particle that enters the instrument but is not detected by the mass spectrometer due to any of these three loss terms contributes to the mass discrepancy between the AMS and another (perfectly calibrated) mass measurement.

Previous measurements and models have characterized the loss of particles in the lens region and orifice, and have shown near-unit transmission efficiencies for particles in the size range of 60–600 nm. However, for particle populations whose distribution is significantly outside of the transmission window, especially for larger particles, $E_{\rm L}$ can contribute significantly to CE_m (Quinn et al., 2006). The striking efficiency is a measurement of the divergence of the particle

beam upon expansion into the particle time-of-flight (PToF) chamber. While spherical particles can be narrowly focused on the 3.8 mm wide vaporizer over the distance of the PToF chamber, non-spherical particles can diverge from the focused beam, causing sub-unit values of E_S (Huffman et al., 2005). Studies show this term accounts for very little particle loss for ambient aerosol (Salcedo et al., 2007), as well as laboratory SOA and (NH₄)₂SO₄ (Docherty et al., 2013). E_S can be well characterized by the use of a beamwidth probe (Huffman et al., 2005).

In the majority of cases, the largest uncertainty and largest contributor to sub-unit CE_m is the particle bounce term, E_B . Particle bounce has long been known to confound particle measurements, such as impactors and surface-desorption mass spectrometers (e.g., Myers and Fite, 1975; Virtanen et al., 2010). A limited number of studies have investigated the nature and root cause of particle bounce for laboratory aerosols in the AMS. Alfarra (2004) identified particle phase state as a controller of particle bounce for a selection of laboratory organics, where particle phase state was inferred from the room temperature properties of the bulk materials. Liquid particles had near-unit CE_m, while solid particles had much lower efficiencies ($CE_m = 0.2$ to 0.5). Matthew et al. (2008) found phase state to govern particle bounce as well. Ammonium nitrate particles, thought to be metastable liquids at their experimental conditions (Lightstone et al., 2000), displayed high CE_m, while dry ammonium sulfate particles had $CE_m = 0.22$, which increased to 0.73 when the particles were hydrated and deliquesced. Matthew et al. (2008) also found that CE_m for dry ammonium sulfate increased as the thickness of a liquid dioctyl sebacate coating layer increased. In some chamber experiments, Bahreini et al. (2005) showed this same increase in CE_m for dry ammonium sulfate particles with condensation of an SOA layer. However, for other SOA experiments, CE_m for ammonium sulfate seed particles actually decreased with the condensation of SOA, implying that the SOA phase state was highly variable in their experiments and/or that other factors also govern particle bounce in the AMS, such as composition or volatility. Similarly, Robinson et al. (2015) showed that CE of liquid squalane (CE \sim 1) particles decreased following SOA condensation. Docherty et al. (2013) report an inverse relationship between CE_m for chamber-generated SOA and the f_{44}/f_{57} ratio (where m/z 44 is comprised of CO₂⁺, while m/z 57 is comprised of the less oxidized marker fragments $C_4H_0^+$ and $C_3H_5O^+$, and f_i is the fraction of m/z_i to the total organic signal). This implicates oxidation state as either a factor influencing CEm or a proxy variable for what makes a particle bouncy.

An even smaller number of studies have used the lightscattering single-particle (LSSP) module of the AMS to investigate collection efficiency, despite its ability to provide a real-time, particle-number-based measurement of $E_{\rm B}$. When $E_{\rm S}$ and $E_{\rm L} \sim 1$, collection efficiency is equal to the bounce efficiency (CE $\sim E_{\rm B}$). We denote this number-based collecE. Shipley Robinson et al.: α-pinene SOA collection efficiency using LS-AMS

tion efficiency as CE_p for "particle collection efficiency", which is defined as

$$CE_{p} = \frac{Particles with ion signal above threshold}{All particles detected by LS}.$$
 (3)

Cross et al. (2007) first introduced LSSP as a method to resolve real-time densities of externally mixed aerosols. Cross et al. (2009) later described the ability of LSSP to measure CEp for ambient particles from Mexico City and found that a significant fraction of the optically detected particles were either undetected by the mass spectrometer due to bounce (hereto referred to as "null") or exhibited signal at a time much later than would be expected based on their in situ measured velocity (referred to as "delayed"). "Prompt" particles, those that gave an appreciable chemical ion signal when they were expected to do so, made up only 23 % of the measured aerosol, with the delayed fraction at 0.26 and the null fraction at 0.51. Liu et al. (2013) also report CEp for ambient measurements taken in Bakersfield, CA (Cal-Nex). They report a 0.46 prompt fraction, 0.06 delayed, and 0.48 null, and found a slight size dependence in the campaign-average CE_p, which exhibited a maximum around $d_{va} = 600 \text{ nm} (0.52)$ and a minimum (0.42) for large particles. Slowik et al. (2009) compared CE_m (density-corrected scanning mobility particle sizer (SMPS)-AMS comparison) and CEp for an ambient biogenic SOA event, and found them to be equal.

Here we further explore the use of LSSP to identify the nature of collection efficiency for lab- and chamber-generated aerosols. We quantify particle bounce for SOA from α pinene ozonolysis, as well as ammonium nitrate, ammonium sulfate, and d_{62} -squalane. We illustrate the difference between mass-based and number-based CE, which are not necessarily the same even for monodisperse aerosol, due both to decreasing effective ionization efficiencies for delayed particles (defined as ions per particle, or IPP) and mass that registers at the detector on timescales much longer than the chopper cycle. We show that IPP decreases with delay time, that CE_p is not a function of size for the SOA in this study, and that low-volatility and/or high oxidation state decreases CE_p for SOA.

2 Methods

2.1 Particle generation and sampling

We prepared inorganic aerosols (ammonium nitrate, ammonium sulfate) by atomizing dilute solutions (1 g L^{-1}) using a constant output nebulizer (aerosol generator model 3076; TSI, Inc.). We sent these particles through a krypton neutralizer (10 mCi) and then size-selected them using a differential mobility analyzer (DMA; classifier model 3080; TSI, Inc.) before sampling.

We sampled size-selected SOA in this same manner, but with a different preparation procedure. We injected a $1.2 \,\mu$ L

aliquot of α -pinene (Sigma Aldrich, >99%) into a clean and dry (RH < 3%) 100 L Tedlar sample bag (SKC, Inc.) at an estimated mixing ratio of ~ 2 ppm and charged the bag with excess ozone. This SOA formed at a high concentration ($C_{OA} \approx 1500 \,\mu g \,m^{-3}$). This allowed us to study homogeneously nucleated SOA with the single-particle capability of the AMS, as the scattering laser requires large ($d_{va} \ge 180 \,m$) particles. However, the composition of SOA is loadingdependent, as demonstrated by Shilling et al. (2009), and so preparing SOA at this necessarily high concentration is a potential limitation of this work, as is often the case for laboratory studies of SOA systems. See Fig. 1 for the general experimental schematic.

We produced d_{62} -squalane aerosols directly in the 12 m³ Carnegie Mellon University smog chamber, described elsewhere in greater detail (e.g., Robinson et al., 2015). In brief, we flushed the smog chamber continuously for > 12 h with clean, dry air (cleaned with HEPA, silica-gel, and activatedcarbon filters in series) to ensure low background particle, organic vapor, and water vapor concentrations. We prepared d_{62} -squalane particles by an evaporation–condensation process within the smog chamber, using a small, resistive stainless-steel heater in situ. We placed a small aliquot of d_{62} -squalane (0.75 µL) on the heater surface, which we then inserted into the smog chamber. Clean dispersion air flowed over the heater to carry and mix the d_{62} -squalane vapor plume into the chamber while we power-cycled the heater for 10 min. Pure d_{62} -squalane particles formed as the squalane vapor plume cooled.

We measured ensemble particle volume and number concentrations using a SMPS (TSI, Inc.). We measured ensemble composition and mass with the high-resolution time-offlight aerosol mass spectrometer (HR-ToF-AMS; Aerodyne, Inc,) operated in single-reflectron V-mode, fully described by DeCarlo et al. (2006). We acquired single-particle mass spectra using the LSSP module coupled to the HR-ToF-AMS. We analyzed single-particle AMS data using Sparrow $1.04D^1$ and ensemble AMS composition data using SQUIR-REL 1.51^2 .

Thermodenuder experiments were conducted using the Aerodyne thermodenuder (TD), based on the design of Huffman et al. (2008, and fully detailed therein). Briefly, the TD consists of a heating section followed by a cooling diffusion denuder section to prevent recondensation. The TD temperature is controlled by proportional–integral–derivative (PID) controllers that adjust the power of three different strips of

¹Sparrow 1.04A, written by D. Sueper, Aerodyne Research Inc. and University of Colorado at Boulder; available at http://cires1.colorado.edu/jimenez-group/ToFAMSResources/ ToFSoftware/#Sparrow

²SQUIRREL 1.51, written by D. Sueper, Aerodyne Research Inc. and University of Colorado at Boulder; available at http://cires1.colorado.edu/jimenez-group/ToFAMSResources/ ToFSoftware/#Analysis2



Figure 1. Experimental setup for SOA CE experiments.



Figure 2. Ensemble mass distributions from SMPS (black trace, adjusted for density) and AMS (green trace) of size-selected α -pinene-derived SOA particles with 370 nm mobility diameter for an example SOA experiment. Frequency of optically counted particles (from LSSP) as a function of size shown in blue. For this instance, $CE_m = 0.39$. The blue trace is normalized to 1 and plotted on the right axis so as to have the same height as the SMPS trace, reflecting that optical detection in the AMS flight chamber is not affected by particle bounce.

heating tape according to temperature measurements from three thermocouples inserted into the center of the TD tube. The ramp program increased temperature linearly over 1 h from 27 to 130 °C, soaked at 130 °C for 10 min, and then returned back to 27 °C at the same rate. Residence time in the heating section (calculated based on plug flow through the TD tube at ambient temperature) was ~ 30 s, which was determined by the combined flow rates of the AMS and SMPS.

2.2 Operation of light-scattering module

The LSSP module has been described in detail elsewhere in the literature (Cross et al., 2009). Briefly, the LSSP module consists of a continuous-wave laser (405 nm, 50 mW; LC BCL-050-405; CrystaLaser) that crosses the collimated particle beam within the time-of-flight region of the AMS. Scattered light from sampled particles is collected by an ellipsoidal mirror that focuses the light onto a photomultiplier tube. This light-scattering signal constrains the particle's velocity between the opening of the AMS chopper and the laser, allowing for the calculation of the vacuum aerodynamic diameter. It also prompts collection of individual mass spectra over the entire chopper cycle (e.g., 200 spectra/chopper), allowing for the identification of signals from individual particles within the full chopper cycle. Saving at this data rate without the laser triggering (meaning all chopper cycles, not just ones containing particles) is not practically useful, as it results in an unmanageable data load. For example, when Drewnick et al. (2005) collected ToF-AMS single-particle data without any triggering mechanism, of the 2.41 GB of data they collected, only 4 MB represented meaningful single-particle spectra after applying their thresholding algorithm. The LSSP enables continuous single-particle detection at a high duty cycle for the long timescales of chamber studies or ambient sampling.

For data processing, we used an operationally defined light-scattering threshold of five (signal-to-noise ratio, SNR) to identify particle events and a mass threshold of six ions to identify a detected particle to be further considered for particle classification, similar to Liu et al. (2013). For ammonium sulfate, ammonium nitrate, and SOA, we used Sparrow's default ion list (*m*/*z* 15, 30, 35, 36, 41, 43, 46, 48, 55, 57, 64, 71, 73, 80, 81, 98) for identifying particle events in the mass spectra of each chopper cycle. We used a different list of deuterated ions (m/z 48, 50, 66, 82, 98) to identify MS events for d_{62} -squalane particles. We processed a subset of SOA experiments with an adjusted ion list based on the 13 highest-signal ions for SOA that do not have significant background interferences identified with MS mode spectra (m/z 15, 26, 27, 29, 41, 42, 43, 44, 53, 55, 65, 67, 69, 79),but our collection efficiency results were not sensitive to this change.

At the number concentrations of the high- C_{OA} SOA experiments, coincident particles – multiple particles sampled in a single chopper cycle – were present (13 % of particles were coincident). We identified and filtered out coincident particles (identified by multiple instances of threshold crossing,

where the threshold was equal to 5SNR of the scattered light trace) using the Sparrow analysis program. Coincident particles were not considered in our analysis or calculation of CE_p . It should be noted that, in the case where two or more particles enter the same chopper cycle and are also the exact same size, the LS data analysis program fails at identifying coincidence. However, even at the highest number concentrations used in these experiments, we estimate the probability of failing to identify these particles as coincident to be 0.4 %. Thus, we do not expect these false negatives to effect the results stated in this paper. For low number concentrations, e.g., those of typical smog chamber experiments, the chance of failing to identify coincidence is essentially zero.

2.3 Calculation of collection efficiency

We classified individual particle events based on how they interacted with the vaporizer, in terms of both their effective ionization efficiency and vaporization quickness. Null particles are those that do not exceed the six-ion mass threshold, despite being identified as a particle event by exceeding the light-scattering threshold. As defined in Cross et al. (2009), particles categorized as prompt arrive at the mass detector within a narrow time range after they would be expected to arrive based on their measured velocity in the PToF region and assuming instantaneous vaporization/ionization. The operationally defined boundary between the prompt and delayed particles is when the actual arrival of the mass signal is greater than the expected arrival time by 20% or more. In other words, we compared the measured arrival time at the detector (MS arrival) and the LS-estimated arrival time (LS arrival) based on the measured velocity between the chopper and laser to draw the boundary between prompt particles (MS arrival/LS arrival < 1.2) and delayed particles (MS arrival/LS arrival > 1.2). As we shall show, this particular value for determining the boundary between prompt and delayed particles is arbitrary.

LSSP provides an internal number-based measure of the AMS collection efficiency (Cross et al., 2009). The wide laser beam (≈ 2 mm), relative to the width of the particle beam (≈ 0.5 mm), allows for near-complete optical detection of particles above the detection limit of the laser ($d_{va} > 180$ nm). The LSSP-based CE_p is the comparison between the optically detected particles (i.e., all particles that enter the PToF region and that will hit the vaporizer surface) and the number of particles that are chemically detected (i.e., give signal in the mass spectrometer). For all particles sampled here, E_S and E_L are reasonably assumed to be 1. Thus, in terms of the categories prompt, delayed, and null, the general definition of CE_p from Eq. (3) can re-written as

$$CE_{p} = \frac{N_{prompt} + N_{delayed}}{N_{prompt} + N_{delayed} + N_{null}},$$
(4)

where, e.g., N_{prompt} is the number of prompt particles. In this formulation, we consider both prompt and delayed particles

as those that give meaningful chemical signals at the detector, though it may be of interest in other studies to look at the CE_p from, e.g., only prompt particles. We are equating CE_p with E_B , a reasonable assumption for the aerosols studied here as they all fall within the lens transmission window $(E_{\rm L}=1)$ and are spherical (Zelenyuk et al., 2008) and therefore do not exhibit significant divergence from the particle beam ($E_{\rm S} = 1$). However, it is important to note this collection efficiency accounts only for whether or not a particle was observed in the mass spectrometer and does not account at all for signal strength above the detection threshold. Additionally, while null particles do not count as meaningful in the LSSP determination of collection efficiency, the sum of many very weak signals from many null particles can result in meaningful mass in the more typical bulk measurement mode (MS mode) of the AMS.

3 Results and discussion

3.1 Delayed vaporization PToF artifact

It is standard practice to present comparisons between the mass-weighted size distribution from the SMPS and the PToF mass distribution from the AMS to compute density and collection efficiency (DeCarlo et al., 2004; Kostenidou et al., 2007; Shilling et al., 2009). The SMPS size distribution is multiplied by the density to align the mode diameters according to

$$d_{\rm va} = \frac{\rho_p}{\rho_0} \frac{d_{\rm ve}}{\chi},\tag{5}$$

where ρ_p is particle density; ρ_0 is standard density (1 g cm^{-3}) ; and χ is the dynamic shape factor, which is equal to 1 for spherical particles and is assumed to be true in the case of SOA from α -pinene ozonolysis (Zelenyuk et al., 2008). For spherical particles, d_{ve} , the volume-equivalent diameter, is equal to mobility diameter.

For this example experiment, where 370 nm SOA particles were size-selected using a DMA, shown in Fig. 2, we estimate the density to be 1.1 g cm^{-3} from aligning the mode diameters of the SMPS-calculated mass distribution with that from the AMS mass distribution measured in PToF mode. The shaded blue area is the frequency of optically counted particles as a function of size, as measured by light scattering in the AMS. Like the SMPS distribution, this histogram is tight, as we expect it to be for size-selected particles. However, even after shifting the SMPS distribution by the density, the agreement between the SMPS and AMS PToF distributions degrades considerably at large diameters.

We explore the nature of the divergence between the AMS PToF mass distribution and the SMPS-derived mass distribution at large apparent diameters using data from LSSP mode. We show the flight path, and resulting data, for a particle in



Figure 3. Illustration of LS and MS signals for a typical delayed single particle in AMS. Scattered light signal (teal) and mass spectrometer signal (orange) as a function of particle time of flight for an example delayed particle. The particle velocity (v_{LS}) is calculated by the measured time between the start of the chopper cycle (point A) and detection of the scattered light peak (B). The velocity is used to estimate an expected arrival time of the chemical ion signal at the mass spectrometer (C) assuming prompt evaporation and ionization of the particle at the vaporizer. The difference between the expected (C) and actual (D) arrival times is denoted by δ and allows for the operational definition of prompt and delayed particle events.

the LSSP AMS in Fig. 3 (similar to Fig. 7 in Cross et al., 2009). The scattered light pulse (teal trace) triggers acquisition of mass spectra over the entire chopper cycle. Individual extractions from the mass spectrometer, which are averaged together over tens of seconds to minutes in typical bulk mode operation, are resolved at $\sim 30 \,\mu s$ (the ToF-MS pulser period) in single-particle mode (orange trace). Using the distance between the chopper and the point of intersection between the laser and particle beams, a flight velocity is calculated and used to predict the arrival of the particle's ions at the mass detector, assuming instantaneous vaporization and ionization. We show the mass signal as a function of time of flight for the chopper cycle in orange. For some particles, the arrival of the ions at the detector is significantly offset (delayed) from the predicted arrival time. This offset (labeled " δ " in Fig. 3) is used to categorize particles into prompt and delayed categories, further discussed in Sect. 2.3.

Figure 4 shows total ion signals from individual particles (gray circles) along with total summed signals of prompt (blue) and delayed (red) particles as a function of time of flight. We see that the large-diameter PToF tail (green) collected in AMS PToF mode matches the delayed particle distribution. Additionally, none of the prompt particles have measured times-of-flight greater than 4 ms. As described in Cross et al. (2009) for ambient OOA measured in Mexico City, the physical basis for the broadened PToF distribution at



Figure 4. Size distribution comparison between bulk PToF and prompt and delayed single particles. Particle signal versus particle time of flight from the chopper to the mass detector is shown for ensemble mode (green trace) and for all detected single-particle events (gray circles) in a representative SOA experiment (DMA size-selecting SOA particles with mobility diameter = 370 nm). Particles are sorted into either prompt or delayed categories based on their delay time. The mass signals for individual particles within each category are binned by flight time and summed to create the prompt (blue trace) and delayed (red trace) distributions.

large diameters is particles with delayed vaporization, which comprise a significant fraction of the measured single particles in this SOA experiment (19 % of all particles). However, the mechanism of the delayed vaporization has not yet been fully described for SOA from α -pinene + O₃.

3.2 Collection efficiency

The average CE_p across all SOA experiments was 0.30 (±0.04), while the average CE_m was 0.49 (±0.07). We calculated CE_m using Eq. (1), where S_{AMS} is the AMS-measured mass from MS mode and S_O is the density-corrected SMPSmeasured mass. Like Cross et al. (2009), we see that CE_m $> CE_p$, which likely reflects two differences between the mass-based and particle-based collection efficiencies. First, by definition, null particles in LSSP mode, those which do not register mass above the six-ion threshold, provide no chemical information. LSSP can only tell us that these particles bounced away from the vaporizer. However, there are examples (e.g., Huffman et al., 2009) where particulate mass is detected by the AMS on very long timescales (5 s) compared to the length of the chopper cycle window (5 ms). While a particle defined as null provides no chemical information whatsoever in LSSP mode, it is likely that not all null particles are created equal: some bounce away from the vaporization/ionization region altogether and are not measured at all, while some bounce from the vaporizer cone but still do evaporate at very long timescales relative to the chopper cycle. Evidently, the sum of some number of these particles from the null category does result in detectable mass on timescales



Figure 5. Histogram of ions per particle for null, delayed, and prompt SOA particles. Histogram of ions per particle for null (gray), delayed (red), and prompt (blue) particle categories for 370 nm SOA particles. The *y* axis is the frequency of single-particle events within each category (in other words, all data for each category sum to 1). The histogram bars for the delayed category are offset (by five ions) on the *x* axis for clarity.

longer than the chopper cycle, as evinced by CE_m being significantly greater than CE_p .

Secondly, some particles that would register mass above the LSSP threshold may be delayed such that their mass signal registers at the detector just beyond the chopper cycle. As depicted in Fig. 4, the delay times for some particles are just beyond the chopper cycle window that we used for these experiments, as there are still mass signals arriving at the very right edge of the plot where the cycle ends. It should be noted that the length of the chopper cycle used in these experiments was not optimal and that a longer cycle would allow us to see the most-delayed particles. We recommend a long chopper cycle for ambient measurements and/or any experiments where delayed particles may be expected. For aerosol types with a high delayed fraction like this SOA, a longer chopper cycle would better accommodate these particles with long (2 ms) delay times. Thus, while LSSP provides an in situ measurement of the AMS collection efficiency, it is important to distinguish between the LSSP-based (Eq. 4) and mass-based (Eq. 1) calculations of collection efficiency.

3.3 Delayed particle signal strengths

Despite nearly equal numbers of prompt $(17\% \text{ of all par$ $ticles})$ and delayed particles (19% of all particles) for this SOA, these two particle categories do not contribute equal mass signal to the detector. As shown in Fig. 5, prompt particles produce significantly more signal per particle than delayed particles even though they are all the same nominal size. We plot in Fig. 5 a histogram of IPP, normalized so that the sum of the bins for each category is 1. This figure shows that the effective ionization efficiency for prompt par-



Figure 6. Average ions per particle as a function of delay time for SOA. Ions per particle as a function of the delay time between the expected time of arrival for the chemical ion signal and the actual time of arrival for 370 nm SOA particles. The data points are the arithmetic mean IPP value for a given delay time bin. Error bars are the standard error of the mean for each bin, which represent the precision of the average IPP values. The gray shadow behind is the standard deviation of ions per particle within each bin, which reflects the inherent spread of single-particle signals at a given delay time for monodisperse SOA. Dotted line shows the average IPP for the entire ensemble, while the solid line shows the calculated IPP based on an ionization efficiency (IE) of 5e-7 and an RIE of 1.4 for organics compared to ammonium nitrate. We also estimate the nominal distance bounced (top x axis) for these particles, assuming completely elastic collisions with the vaporizer and surrounding surfaces and the average velocity of the size-selected particles measured between the chopper and laser.

ticles is higher than that of delayed particles. Note that this "effective" ionization efficiency is not only a function of the ionization efficiency of the molecules being ionized by the 70 eV source (a molecular property), but it also convolves the instrument sensitivity to particles that may be vaporized in a sub-optimal location (for ion formation and extraction). If delayed and prompt particles had the same IPP, the delayed vaporization tail in the AMS mass distribution for SOA shown in Fig. 2 would be even more pronounced.

The single-particle mass signal (IPP) is a smooth function within both the prompt and delayed categories, possibly providing reason to redefine what it means to be prompt vs. delayed. Figure 6 shows a steady decrease in the average IPP as a function of delay time for delays shorter than 1 ms. For delay times longer than 1 ms, the IPP is constant with delay time. The error bars represent the standard error of the mean within each bin, while the gray shadow shows the standard deviation for each bin reflecting the inherent spread of single-particle mass signals. For comparison, we include on the plot the average IPP value across all prompt and delayed particles, which is very similar to its calculated value based on the calibration IE and a RIE value for organics of 1.4.



Figure 7. Cumulative particle counts as a function of delay time for SOA, NH_4NO_3 , $(NH_4)_2SO_4$, d_62 -squalane, and SOA. (a) Cumulative probability distributions of particle counts as a function of delay time for ammonium nitrate (blue), d_{62} -squalane (purple), ammonium sulfate (red), and SOA (green). All traces are normalized by the respective CE_p values, which are the average value across all experiments for that particle type. (b) Cumulative probability distributions for single-particle counts (dark green) and single-particle mass (light green) for an individual SOA experiment. The dark green trace is scaled by CE_p . The light green trace, up to 2.5 ms delay time, is scaled by the mass collection efficiency as determined by comparing the AMS-PTOF-determined mass to the SMPS mass (denoted CE_m '), according to Eq. (1). The broken axis represents additional mass seen beyond the window of the chopper cycle, and that mass is scaled according to the mass collection efficiency determined by the AMS mass seen in MS mode compared to the SMPS mass (CE_m).



Figure 8. Mass spectral signal profiles for two (prompt and delayed) PToF arrival times for SOA. Profiles of single-particle mass arrival for SOA (**a**) and ammonium nitrate particles (**b**) under different vaporization scenarios. (**a**) Plot shows total chemical ion detection as a function of time from arrival of maximum signal for SOA. The traces represent the average signal for all particles with the same MS arrival time. The two arrival time bins shown correspond to either all prompt (PToF bin = 3.21 ms, blue trace) or delayed (PToF bin = 4.05 ms, red trace) particles. N is the number of particles used to make the average trace. (**b**) Similarly, average chemical signals as a function of arrival time are shown for ammonium nitrate particles at two different vaporizer temperatures. The arrival of mass at the detector (event length) is significantly longer for ammonium nitrate at 200 compared to $600 \,^{\circ}$ C.

It should be noted here that, as is done in most analysis of AMS data, converting from the nitrate-equivalent mass to the absolute mass measurement for a given non-refractory species (e.g., organics, sulfate, chloride) requires the application of species-specific values of both CE and RIE (see, e.g., Eqs. 3.8 and 3.9 in Alfarra, 2004). Thus, any measurement of CE also has inherent value regarding understanding RIE for a given species. Figure 6 illustrates this, as the measured average IPP for all particles matches the calculated value. However, clearly the least and most delayed particles have IPPs much different than the average, and thus particle bounce and the associated loss of signal significantly affect IPP for a given particle. Measurements of RIE for various species using the AMS – as have been reported by, e.g., Mensah et al. (2011), Silva et al. (2008), and Jimenez et al. (2016) – are only possible when CE for the sampled aerosol particles is well known. Given that LSSP measures CE inherently, easier and more routine measurements of species-specific RIE values, especially in ambient datasets, should be made possible with application of the LSSP module.

Plotting the accumulated particle counts as a function of delay time shows how single-particle information from LSSP mode can be used to best understand the response of the AMS to different particle types, each with its own sensitivity in the instrument (Fig. 7). We scale the traces in Fig. 7a by their measured CE_p values (from Eq. 4). The effect of delay time on IPP is absent for ammonium nitrate, the standard mass calibrant for the AMS, because all particles arrive within the first few delay time bins. D₆₂-squalane, a liquid at room temperatures with a near-unit CEp, largely accumulates its signal at small delay times as well but is slightly slower to do so than ammonium nitrate. We speculate that this difference may be attributable both to the lower volatility of d_{62} squalane and to the larger molecular weight of d_{62} -squalane (423 g mol^{-1}) compared to ammonium nitrate (80 g mol^{-1}) . We estimate the d_{62} -squalane vapor pressure using SIMPOL (Pankow and Asher, 2008) and use the ammonium nitrate vapor pressure reported by Richardson and Hightower (1987): ammonium nitrate is more volatile than d_{62} -squalane (~30 and $\sim 0.1 \,\mu g \, m^{-3}$, respectively). Saleh et al. (2016) calculated the differences in evaporation timescales in the AMS vaporizer for species of different volatility, while Murphy (2015) discussed the molecular weight dependence on the movement of ions from the ion source to the ion optics region in a free molecular regime. Unlike both ammonium nitrate and d_{62} -squalane, which accumulate signal at very short delay times despite their differences, SOA exhibits substantial delayed vaporization and low CEp. The SOA in this study behaves similarly to crystalline ammonium sulfate, a possible indication of a solid or semi-solid phase state, extremely low-volatility material, or both.

Figure 7b shows how the total mass signal from single SOA particles accumulates faster than the particle counts as a function of delay time, as particles with low delay times contribute relatively more mass signal on average. The accumulation of single-particle counts is scaled by CE_p , while the single-particle mass accumulation trace is scaled by CE_m . We use CE'_m to denote the mass collection efficiency calculated by comparing the AMS PToF vs. SMPS mass, and CE_m to denote the mass collection efficiency calculated according to Eq. (1). The difference between CE'_m and CE_m is the amount of mass measured at timescales longer than the chopper cycle.

3.4 Nature of particle–vaporizer interactions

These results seem to indicate that, when an aerosol type exhibits bounce, it also exhibits delayed vaporization and thus lower effective ionization efficiency for some fraction of particles. In investigating the offset between expected and actual arrival times, we tested two ideas about how the signal at the mass detector would arrive for SOA within the LSSP chopper cycle. If an SOA particle strikes and adheres to the vaporizer surface but does not promptly vaporize, it should show an accumulation of mass at the detector over time, beginning at the expected arrival time. However, if the particle bounces off the vaporizer without any significant evaporation and somehow returns to a hot surface at a later time, then the time-resolved arrival of ions should look similar to a prompt particle that vaporizes upon impact, albeit after some time associated with its bouncy journey.

Indeed, when the mass arrival signals for an ensemble of single-particle events are averaged together, we see that prompt and delayed SOA particles have the same peak shape (Fig. 8a). Here, we display the average single-particle mass signal for particles with the same arrival time. We chose two arrival-time bins with times-of-flight equal to 3.21 and 4.05 ms. All particles in each bin are categorized as prompt and delayed, respectively. The similar, sharp peak shape suggests that delayed particles are truly delayed in starting their vaporization process and not simply evaporating at a slower rate. Drewnick et al. (2015) present the vaporization "event length" quantity, which is the full width at half maximum (FWHM) of mass arrival signals from individual particles. In our study, the time resolution of the mass arrival trace (determined by the pulser period, 30 µs) is on the same order as the event length, which does not allow us to quantify the event length with any precision. It should be noted that the pulser period used in this work is a limitation; a faster pulser period should be used for future similar work, as it would allow for proper quantification of the event length. However, qualitatively we can say that prompt and delayed particles for the SOA presented here have similar event lengths and are on the order of $\sim 30 \,\mu s$, similar to those measured by Drewnick et al. (2015) for ammonium sulfate aerosol. We found nearly identical event lengths for prompt versus delayed ammonium sulfate as well, indicating that ammonium sulfate exhibits the same behavior of "flash vaporizing" even when the particles are delayed. The event length for ammonium nitrate aerosol at low vaporizer temperatures, however, is fundamentally different (see Fig. 8b); mass arrives over a much longer timescale (1 ms), indicating that particles are sticking to the vaporizer and slowly losing mass. Thus we conclude that delayed SOA, as well as ammonium sulfate, particles are bouncing around the ionization cage after initially striking the front of the vaporizer before they finally land and flash-vaporize on one of the hot surfaces in the vaporization region (e.g., side of the vaporizer, ionization cage). Our conclusion is the same as that of Cross et al. (2009), who identified this mechanism acting on delayed particles in ambient measurements in Mexico City.

The AMS vaporizer is a cylindrical tube furnace (r = 3.81; l = 20 mm) with a concave beveled cone (60° included angle) serving as the stop for the particle beam. It is centered within an ionization cage, a rectangular stainless-steel housing (h = 6; w = 8; l = 15 mm) which is open on each end.

The front end of the vaporizer is set back $\sim 10 \text{ mm}$ from the front opening of the ion cage and $\sim 2 \,\mathrm{mm}$ from the ion extraction volume, maximizing the intersection of the vaporized particle plume, the electron beam from the filament, and the axis of ion extraction. Because of the long hot surface of the vaporizer, which is housed inside a sheet metal cage, this mechanistic picture of particles bouncing around this region before finally landing on a hot surface is plausible. Importantly, for this SOA, the actual vaporization of the particle still can be thought of as rapid – when the particle finally does stick, it is vaporized and ionized on the same timescale as a prompt particle. Thus, the "PToF broadening" shown in Fig. 2 can be attributed to SOA particles bouncing around before vaporizing, not slowly boiling off adsorbed material over time, as discussed in Salcedo et al. (2010) for lead salts (e.g., PbCl⁺) and in Drewnick et al. (2015) for sea salt and other semi-refractory components (e.g., ZnI₂). Furthermore, this explanation is consistent with the decrease in IPP as a function of delay time: when particles vaporize on, e.g., the side of the vaporizer, they are in a sub-optimal position for ionization of the resulting vapor plume and thus detection of the full single-particle mass (Huffman et al., 2009). From Fig. 6, the decrease in IPP with delay times up to 1 ms indicates an increasingly sub-optimal average vaporization location for the particle with respect to the ionization region. For long delay times (>1 ms), the likelihood of the particle landing near the ionization region becomes very low, but further delay does not influence the effective ionization efficiency. As indicated by a wide spread of IPP values for a given delay time in Fig. 6, it is very unlikely that a long-delayed particle can provide as many ions to the mass detector as the average prompt particle can.

In Fig. 6 we also show a secondary x axis of distance bounced based on the nominal particle velocity. This is the distance traveled after the initial particle impact on the vaporizer, assuming elastic scattering as the particle bounces. Work by Xu et al. (1993) and Miyakawa et al. (2013) shows that there are velocity losses for submicron particle collisions with surfaces, though the range of velocity loss appears to be a complex function of particle composition, incident angle of the collision, and other factors. Thus, while our assumption of completely elastic collisions is flawed, it does provide a back-of-the-envelope measure of the upper limit of distance bounced by these particles. This inferred distance is much longer than the length scales of the vaporizer and ionization cage. We thus conclude that the particles are probably literally bouncing randomly around the ionization region, impelled by surfaces that are rough at the length scale of the particles. The top x axis of Fig. 6 shows our upper-limit estimate for the nominal distance bounced for these 370 nm particles. We used the average measured velocity of the prompt particles, as measured between the chopper and laser. When comparing the length scales ($\sim 1 \text{ cm}$) of the ionization cage and vaporizer with our estimated distance bounced based on delay times, the most delayed particles experience many collisions with ionizer/vaporizer surfaces before finally vaporizing.

As a further check that the SOA particles measured in LSSP mode are rapidly vaporizing – just simply doing so at a time later than would be expected based on their measured size and expected time of flight - we increased the temperature of the vaporizer from 600 to 800 °C. Were the particles sitting on the vaporizer surface and slowly boiling, we would expect this temperature increase to decrease the broadened PToF tail (Fig. 9a). We do not see this effect (note: the degradation in the organic PToF signal at 800 °C is due to low particle numbers at the end of our experiment due to wall loss). However, when we coated SOA particles with d_{62} -squalane, a liquid at STP and a material that exhibits essentially no particle bounce in the AMS ($CE_p \sim 1$), the broadened tail of the SOA mass distribution diminished, as shown in Fig. 9c. When we heated the chamber, causing the d_{62} -squalane to evaporate, the broadened tail reappeared. This further supports this idea that delayed SOA particles are bouncing around the vaporizer-ionizer region before finally flash-vaporizing (Fig. 9b).

On the other hand, the PToF distribution for ammonium nitrate can be broadened by decreasing the vaporizer temperature from 600 to 200 °C. Figure 9b shows the mass distribution of $m/z \, 46 \, (\text{NO}_2^+)$ for both vaporizer temperatures. The increase in PToF arrival times (which translates to the broadened mass distribution for the dominant mode of particles) with decreased vaporizer temperature indicates that these particles do stick to the surface and have a reduced mass flux at lower temperatures, thus spreading the signal arrival out over time of flight (Fig. 9b). The secondary mode of ammonium nitrate particles shown in Fig. 9b is multiply charged, larger particles. Docherty et al. (2015), operating their vaporizer temperature on a programmed cycle between 200 and 600 °C, also see PToF broadening for nitrate in ambient data. Mass arrival signals from individual ammonium nitrate particles at these low vaporizer temperatures (shown in Fig. 8b) are much longer (event lengths $\sim 200 \,\mu s$, consistent with those measured by Drewnick et al., 2015) than those shown for prompt and delayed SOA particles in Fig. 8a. There seem to be different mechanisms for particle delay both for different operating conditions of the AMS and for different particle types.

Consistent with this proposed mechanism – that delayed SOA particles are bouncing around and vaporizing on surfaces away from the vaporizer cone – there are differences in mass spectra between prompt and delayed particles. Figure 10 shows the difference mass spectrum between prompt and delayed particles for both SOA and ammonium sulfate, both of which exhibit a high delayed fraction. We created average mass spectra for prompt and delayed particles by summing the single-particle spectra for each category and dividing by the number of particles. We then normalized these average spectra by the sum of ions across all m/z, and the difference mass spectra are the normalized prompt MS minus



Figure 9. Ensemble mass distributions of different particle types. (a) Organic mass distributions for α -pinene-derived SOA particles at two different vaporizer temperatures with DMA-selected mobility diameter of 370 nm: 600 (green) and 800 °C (brown). Note: the degraded signal at 800 °C is due to low particle numbers due to smog chamber wall loss, as these data were taken at the end of an experiment where particle number was relatively low. (b) m/z 46 PToF mass distributions for DMA-selected mobility diameter of 300 nm at the standard vaporizer temperature (600 °C, dark blue) and low temperature (200 °C, sky blue). (c) m/z 43 mass distributions from SOA particles at three stages of a mixed-particle experiment: homogeneously nucleated SOA (teal), SOA particles coated with d_{62} -squalane (red), and SOA/ d_{62} -squalane particles after an increase in chamber temperature (purple). Note the disappearance of the delayed tail with the condensation of d_{62} -squalane and the reappearance of the tail with heating despite the decrease in mode diameter.



Figure 10. Difference plots between prompt and delayed average mass spectra for (a) SOA and (b) ammonium sulfate. Plot is prepared by first normalizing each spectrum by the total signal and then subtracting the normalized delayed MS from the normalized prompt MS. Thus, mass fragments with positive values (blue) are enriched in the prompt MS, and those with negative values (red) are enriched in the delayed MS. Error bars are the propagated standard errors of the mean for each population.

normalized delayed MS. Error bars indicate the propagated standard error of the mean at each m/z.

Several fragments are more prominent in either the prompt or delayed mass spectra, colored by blue and red sticks, respectively. For instance, $m/z \, 43$ (mostly $C_2H_3O^+$) is higher and $m/z \, 44$ (CO_2^+) is lower for delayed SOA particles; the acidic fragments $m/z \, 81$ (HSO_3^+) and 98 ($H_2SO_4^+$) are higher in the delayed MS for ammonium sulfate particles, while $m/z \, 48$ (SO⁺) and 64 (SO₂⁺) are higher in the prompt MS for ammonium sulfate. The water ion (H_2O^+) is enhanced in the prompt MS, while ammonia (NH_3^+) is enhanced in the delayed MS for ammonium sulfate particles. We attribute these differences in mass spectra between prompt and delayed particles to the wide range of possible temperatures experienced by delayed particles that have bounced away from the center of the AMS vaporizer. The lower temperatures at these sub-optimal vaporization positions (e.g., side of the vaporizer, on the ion cage) can lead to different thermal decomposition pathways, which could be important for interpreting ambient single-particle spectra.

To support this hypothesis, we look at previous work conducted by Docherty et al. (2015). They show that acidic fragments from ambient ammonium sulfate measured during the Study of Organic Aerosols at Riverside (SOAR-2005) are enhanced when they lower the AMS vaporizer temperature from 600 to 200 °C, which is consistent with our hypothesis that delayed ammonium sulfate particles were vaporizing on cooler surfaces. Docherty et al. (2015) also show that ambient OA in SOAR-2005 appeared more oxidized at lower vaporizer temperatures, as indicated by increased f_{44} and



Figure 11. Collection efficiency of SOA as a function of D_{va} and thermodenuder temperature. (a) Particle collection efficiency as a function of D_{va} for all SOA experiments. Data are from both size-selected experiments (crosses) and polydisperse SOA from a smog chamber (circles), with each color representing a separate experiment. (b) Particle collection efficiency for 370 nm size-selected particles (colored markers) as a function of thermodenuder temperature for an example SOA experiment, colored by the fraction of m/z 44 (f_{44}) to the total organic mass measured in MS mode. Confidence intervals (95 % CI) for a linear fit are shown (slope: $-0.0020 \,^{\circ}\text{C}^{-1}$).

increased O:C. While f_{44} is slightly higher in our prompt SOA MS, perhaps indicating that the prompt particles appear more oxidized, the rest of the mass spectrum shows that the delayed particles are enhanced in oxidized fragments, while the prompt particles are enhanced in reduced fragments. We see an enhancement in the delayed MS of $C_x H_y O$ fragments, such as m/z 71 (C₄H₇O⁺), m/z 83 (C₅H₇O⁺), and m/z 97 (C₆H₉O⁺). Other studies have found that f_{44} does not change or even decreases with lower vaporizer temperatures than the standard 600 °C; for example, Canagaratna et al. (2015) showed that f_{44} decreases in the MS of *cis*pinonic acid at 200 °C compared to the standard vaporizer temperature. Thus, the enhancement of these $C_x H_y O^+$ fragments in the delayed MS is a more robust indicator than f_{44} that our delayed SOA particles appear more oxidized than the prompt ones. Excluding f_{44} , our data are consistent with Docherty et al. (2015) and the hypothesis that our delayed particles are bouncing around the vaporization/ionization region before landing on cooler surfaces and finally evaporating. Importantly, these data show that particles delayed due to particle bounce, like ammonium sulfate and the SOA studied here, can have differences in their mass spectra that need to be considered when analyzing ambient single-particle data.

3.5 Collection efficiency as a function of size and thermodenuder temperature

As reported previously in the literature, some studies have shown collection efficiency for OA to be size- (Liu et al., 2013) and composition-dependent (Docherty et al., 2013). To investigate any size-dependent collection efficiency that our SOA might have, we selected particles at different mobility diameters with a DMA upstream of the AMS. Figure 11a shows CE_p as a function of selected mobility diameter. LSSP can also provide a size-resolved CE_p for polydisperse aerosol (as in Liu et al., 2013), as each optically counted particle has an estimated d_{va} , estimated from the time of flight between the chopper and the laser. Importantly, this measure of size is unaffected by any vaporization delays and can be compared across LS particle categories (e.g., prompt, delayed, null). Figure 11a also shows CE_p for polydisperse SOA from multiple smog chamber experiments, which agree well with the size-selected data. The CE_p for SOA studied here was not a strong function of size between in diameter range 170– 460 nm. The mean CE_p across all experiments for SOA was 0.3 (±0.04 SD) and ranged from as low as 0.25 to as high as 0.4. Mobility diameters for the monodisperse experiments were adjusted according to Eq. (5), so CE_p vs. size data could be on the same scale.

While CE_p for this SOA is independent of size, we do observe a decreasing trend in CE_p by passing the SOA through a thermodenuder. We sampled SOA alternately through a thermally denuded line, or through a bypass line of the same length held at the same temperature as the chamber. Figure 11 shows CE_p plotted against thermodenuder temperature for an experiment where SOA particles passed through a thermal denuder operating on a temperature ramp profile. Above 110 °C, almost all SOA evaporated in the thermodenuder, making the CE_p values in Fig. 11 are calculated for particles with 200 nm > d_{va} > 300 nm to isolate the effects of volatility and/or oxidation state on CE_p , instead of measuring smaller particles less likely to provide enough detectable mass above the threshold.

We use temperature as a proxy variable for the volatility of the aerosol, because SOA particles that have passed through the denuder will have had some fraction of their more-volatile components removed, the amount of which increases with increasing temperature. We color data points in Fig. 11 by f_{44} as measured from MS mode bulk mass spectra, which is used in AMS analysis as both a direct measurement of oxidation state and a proxy for OA volatility (Ng et al., 2011). These data show that CE_p is inversely related to either the SOA oxidation state, volatility, or both. These results are consistent with the trend shown by Docherty et al. (2013), who saw decreasing CE_m with increasing oxidation state, though they are within the range of scatter shown in Fig. 11a for all SOA experiments. It should be noted that this SOA is similarly oxidized ($f_{44}/f_{57} \approx 6$) and has similar CE_m values (CE_m \sim 0.2–0.4) to much of the SOA in their study. SOA sampled through the bypass line during this same time period did not have any decrease in CE_p. It is not possible to determine whether the decrease in CE_p is attributable to changes in volatility or oxidation state, as the two are coupled in our measurements. However, this example shows that LSSP can be used to verify whether this trend in CE_p with these compositional changes exists for other types of NR- PM_1 .

4 Conclusions

In this study, we present LSSP AMS data that give further insights into the nature of collection efficiency for the common laboratory system of SOA from α pinene + O₃. SOA generated in these experiments exhibited an artificial tail in the PToF distribution at large diameters, which we show to be an artifact of delayed vaporization. By studying the arrival of mass signals for these delayed SOA particles using LSSP data, we see that the signals cannot be attributed to adsorption on the AMS vaporizer followed by slow evaporation. Rather, particles bounce off the vaporizer after primary impact and vaporize on some subsequent impact with a hot surface in the vaporization and/or ionization region. This causes the mass arrival at the detector to be delayed relative to the estimated speed from optical detection but is fundamentally different than slow evaporation from the vaporizer surface. A significant fraction of SOA and ammonium sulfate exhibited this type of delayed vaporization, while ammonium nitrate and d_{62} -squalane exhibited none. For delayed particles, the measured per-particle mass signal is reduced, which we report as ions per particle as a function of delay time. The artificially broadened PToF distributions would be even more prominent if the delayed particles had the same effective ionization efficiency as prompt particles. Some of the SOA particles counted as null evidently evaporate on very long timescales relative to the chopper cycle, as indicated by $CE_m > CE_p$. Null particles register no mass signal in LSSP mode, though what fraction of them will result in detectable mass on the long timescale of MS mode is not discernible using these data. CE_m for SOA across all experiments was 0.49 (± 0.07 SD), while CE_p was 0.30 (± 0.04 SD). We were unThe reduced number of ions per particle of delayed particles means that the AMS PToF signal for polydisperse distributions will be dominated by prompt particles, because larger prompt particles with high IPP will overwhelm smaller delayed particles with lower mass and few ions per unit mass. However, the large diameter tail in AMS PToF distributions should be regarded with caution. Lastly, we use the LSSP to show that particle collection efficiency is not a function of size for the size range of SOA explored ($170 < d_m < 460$ nm) but is related to SOA oxidation state and or volatility.

Rather than being viewed as a limitation, collection efficiency should be viewed as a sensitivity within the AMS that simply needs to be understood for a given system and that may provide additional useful information. We demonstrate here that using the LSSP capabilities of the AMS allows users to gain further insight into a given aerosol system, such as SOA from α -pinene ozonolysis. Further work should be conducted to better understand any compositional artifacts that may be attributable to delayed vaporization for other systems. Data of this kind may also possibly be used for design improvements to the vaporization region.

Data availability. Data used in this study can be made available upon request to the author.

Competing interests. The authors declare that they have no conflict of interest.

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