

Abstract

A new method, near-infrared laser desorption/ionization aerosol mass spectrometry (NIR-LDI-AMS), is described for the real time analysis of organic aerosols at atmospherically relevant total mass loadings. Particles are sampled with an aerodynamic lens onto an aluminium probe and moderate energy NIR laser pulse at 1064 nm is directed onto the probe to vaporize and ionize particle components. Delayed pulse extraction is then used to sample the ions into a reflectron time of flight mass spectrometer for chemical analysis. The soft ionization afforded by the NIR photons results in minimal fragmentation (loss of a hydrogen atom) producing intact pseudo-molecular anions at $[M-H]^-$. The limit of detection measured for pure oleic acid particles (geometric mean diameter and standard deviation of 180 nm and 1.3, respectively) was 140 fg (or 1.7 ng m^{-3} per minute sampling time). As an example of the utility of NIR-LDI-AMS to measurements of atmospheric importance, the method was applied to laboratory chamber measurements of the secondary organic aerosol formation from ozonolysis of α -pinene. High quality mass spectra were recorded with a 2-min time resolution for total aerosol mass loadings ranging from 1.5 to $8.7 \mu\text{g m}^{-3}$. These results demonstrate the potential of NIR-LDI-AMS to allow for more accurate measurements of the organic fraction of atmospheric particulate at realistic mass loadings. Measurements at ambient-levels of SOA mass loading are important to improve parameterizations of chamber-based SOA formation for modeling regional and SOA fluxes and to aid in remediating the discrepancy between modeled and observed atmospheric total SOA production rates and concentrations.

1 Introduction

Atmospheric aerosols have an important role in many atmospheric and environmental processes by exerting an influence on global and regional radiative energy balance, visibility, atmospheric circulation, the hydrological cycle, the regulation of greenhouse

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and reactive gases, and human health (Seinfeld and Pankow, 2003; Kanakidou et al., 2005; Pöschl, 2005). There is surmounting evidence that organic aerosols make a substantial contribution to the total mass of fine aerosols; contributing ca. 20–50% at continental mid-latitudes to 90% in tropical forested areas (Kanakidou et al., 2005). Also, organic compounds may have much higher localized contributions to aerosols during times of high biological activity, as recently observed for marine aerosols (O’Dowd et al., 2004; Meskhidze and Nenes, 2006; Yoon et al., 2007).

Secondary organic aerosol (SOA) makes a significant contribution to the organic fraction and total mass of fine aerosols in the lower atmosphere. As discussed in a recent review on SOA (Hallquist et al., 2009), bottom-up estimates of global SOA production give total biogenic SOA fluxes of 12–70 Tg/yr, and somewhat lower fluxes for anthropogenic SOA. Bottom-up estimates, which combine volatile organic compound (VOC) fluxes with laboratory-derived (e.g. chamber) data, typically estimate global SOA fluxes at about one to two orders lower than values derived from top-down (inverse) estimates, which are based in part on constraining the atmospheric fate of VOC precursors to SOA. The discrepancy in estimating global SOA fluxes between these two approaches highlights the need for a better understanding of the oxidative transformation of VOC precursors to SOA and the gas-to-particle partitioning of these oxidation reaction products. In this regard, there has been a recent call for “an improved understanding of the fundamental processes responsible for SOA formation and how they affect composition, and the design of simulation experiments which more closely reflect the conditions and complexity of the real atmosphere” (Hallquist et al., 2009). The research presented herein addresses these needs by developing an analytical tool of general utility to chamber-based studies that measures SOA as well as primary OA at atmospherically relevant total organic mass concentrations (C_{OA}).

Ambient organic aerosols are predominately composed of oxygenated compounds (i.e. OOA) (Jimenez et al., 2009) and continental levels of C_{OA} are typically less than ca. $10 \mu\text{g m}^{-3}$ (Cabada et al., 2004; Hock et al., 2008; Jimenez et al., 2009); however, traditional organic mass loadings of greater than $15 \mu\text{g m}^{-3}$ are used in most

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chamber-based studies. Most bottom-up estimates of SOA fluxes are based on parameterization of chamber-based SOA formation experiments done at these elevated organic mass loadings not representative of typical ambient concentrations. This limitation may be an important factor contributing to the discrepancy in modeled SOA fluxes between bottom-up and top-down models; moreover, it may, in part, lead to the inability of bottom-up models to explain the observed atmospheric total SOA production rates and concentration.

Several recent experimental studies have shown clearly the importance of characterizing SOA under atmospherically relevant organic particle mass loading. Shilling et al. (2009) characterized SOA particles derived from the dark ozonolysis of α -pinene using an Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) (DeCarlo et al., 2006; Canagaratna et al., 2007) coupled to a continuous-flow chamber. Their study featured a wide-range of organic particle loadings (ca. 0.5 to $>140 \mu\text{g m}^{-3}$) and the mass spectra suggested more oxygenated organic material (i.e. a higher O/C atomic ratio and density) in SOA at lower loading, which also had greater compositional variability compared to higher loadings that are typically employed in traditional chamber experiments. As noted by the authors (Shilling et al., 2009), these experiments suggest that the extrapolation of results derived from chamber-based studies obtained under relatively high loading of the organic particle phase may be inappropriate for modeling SOA formation in the atmosphere where lower loadings are typical.

The high sensitivity, relatively fast time response and low fragmentation afforded by proton-transfer reaction mass spectrometry (PTR-MS) make it an attractive tool for real-time measurements of VOCs in the atmosphere (de Gouw and Warneke, 2006), as well as the monitoring of VOCs and semivolatile organic compounds (SVOCs) in laboratory-based SOA formation experiments (Presto and Donahue, 2006; Ng et al., 2007). For example, Presto and Donahue (2006) coupled PTR-MS measurements of gas-phase VOCs with particle based measurements (i.e. monitored by a scanning mobility particle sizer, SMPS) to investigate SOA production from the ozonolysis of α -pinene at atmospherically relevant total organic mass concentrations (i.e. $C_{\text{OA}} < 10 \mu\text{g m}^{-3}$). The

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results showed that extrapolations of current models to atmospheric C_{OA} levels significantly underestimate SOA under dark, low- NO_x conditions, while conversely, overestimating SOA production under illuminated, higher- NO_x conditions typical of polluted areas. PTR-MS has also been adapted to the measurement of particulate phase organics, for real-time chamber-based studies, albeit at high C_{OA} (Hellén et al., 2008), and very recently for organic particles collected from both chamber-based studies and field observations (Holzinger et al., 2010) by combining PTR-MS with a collection-thermal-desorption (TD) aerosol sampling technique. In this latter study, the reported detection limit of aerosol compounds was 35 pg (or 0.2 ng m^{-3} for a reported aerosol collection time of approximately three hours) (Holzinger et al., 2010) making TD-PTR-MS a potentially powerful tool for the characterization of SOA at low total organic mass loadings.

As has been discussed previously (Noble and Prather, 2000; Hunt and Petrucci, 2002; Nash et al., 2006), a number of different pulsed-laser ionization methods have been used as ionization sources for AMS, including laser desorption/ionization (LDI), which has been coupled with time-of-flight (TOF) mass spectrometry since the early 1990s (McKeown et al., 1991; Mansoori et al., 1994; Prather et al., 1994). LDI is a versatile and highly sensitive ionization source due to the large number of photons per pulse (i.e. irradiance between $\sim 10^6$ to $10^{12} \text{ W cm}^{-2}$) (Hunt and Petrucci, 2002) that can be focused onto a single particle. To date, UV LDI has typically been coupled to AMS (see the aforementioned reviews and references therein), which often results in significant fragmentation of the organic constituents of particles. However, the reduced fragmentation of organic components of particles has been demonstrated by employing infrared radiation for desorption of organic compounds followed by ionization of the vaporized species by UV-radiation in two-step laser desorption/ionization methods (Woods III et al., 2001; Öktem et al., 2004). Small molecule analysis via LDI has been aided by the development of “matrixless techniques” such as DIOS (Shen et al., 2001; Thomas et al., 2001) whereby the surface substrate is thought to act as the matrix absorbing and transferring the laser energy to the analyte. This technique has also been

extended to include metal oxides and metal surfaces (Nayak and Knapp, 2007; Hsu et al., 2008). The following report demonstrates the advantages of surface mediated LDI using single-wavelength near-infrared (NIR) radiation for both desorption and ionization in AMS. The high sensitivity we have observed coupled to the minimal fragmentation of these species makes it an ideal method for the analysis of complex, multicomponent organic particles, including SOA particles.

2 Experimental

2.1 Near-Infrared Laser Desorption/Ionization-Aerosol Mass Spectrometry (NIR-LDI-AMS)

A LDI based aerosol mass spectrometer (Fig. 1) has been developed in which a Liu-type aerodynamic lens (Liu et al., 1995a, b) is used to produce a collimated particle beam, which is directed onto the concave surface of a 1 mm diameter aluminium wire probe (99.9% purity, Alfa-Aesar Chemicals, Ward Hill, MA) held centrally in the ion extraction region of a reflectron time of flight mass spectrometer (R.M. Jordan Inc., Grass Valley, CA). A 100- μm diameter critical orifice (O'Keefe Controls, Monroe, CT) at the entrance of the inlet maintains a constant aerosol sampling flow rate of $83\text{ cm}^3\text{ min}^{-1}$.

Following particle collection for a prescribed time, desorption and ionization are performed by a single 1064 nm laser pulse (5 ns width) produced by a Nd-YAG laser (Brio, Quantel, Big Sky, CO) incident on the surface of the Al probe at approximately 30 degrees from normal. The laser passes through a high energy beam attenuator (935-5-OPT, Newport, CA) offering fine control of the pulse energies and is steered directly into the ionization chamber (i.e. with no additional focusing). The laser spot size is larger than the Al probe surface ensuring small variations in beam direction have minimal effect on the desorption/ionization process. Laser pulse energies are maintained between 25 and 35 mJ per pulse. A separate CW 532 nm laser (Viasho VA-I-N-532, Beijing, China) is aligned in front of the Al wire probe in order to assist with initial

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particle beam alignment, but is not in used during mass spectral measurements.

A pulse generator (DG535, Stanford Research Instruments, Sunnyvale, CA) is used to control the delay time between laser Q-switch trigger and the ion extraction pulsed power supply (PVM-4210, Directed Energy, Inc., Fort Collins, CO). Typical delay times of 5–8 μs are used in order to reduce the high energy ion signals observed to originate directly from the Al wire and to obtain the pseudo-molecular ions of the adsorbed molecules as described below. Mass spectral data was acquired at 1 GS/s with a digital oscilloscope (WavePro 7000, LeCroy, Chestnut Ridge, NY), which currently limits data acquisition to one mass spectrum (i.e., laser firing) per second.

2.2 Particle formation and processing

Pure oleic acid particles were utilized as a proxy for POA. Particles were generated by homogeneous nucleation of oleic acid (Malinckrodt Chemicals, Phillipsburg, NJ) vapor generated in a small flask held at 110 °C and flushed through a condenser by a flow of zero air (USP Medical Air, Airgas East, Williston, VT) into a small, 0.5 m³ Teflon chamber. Aerosol particle number and mass size distributions were measured with a scanning mobility particle sizer (SMPS: Model SMPS 3080, TSI Inc., Shoreview, MN) coupled with a condensation particle counter (CPC: Model 3010, TSI Inc., Shoreview, MN). Aerosol (number) geometric mean diameter and standard deviation were typically on the order of 180 nm and 1.3, respectively.

Secondary particles generated from the ozonolysis of (+)- α -pinene (98%, Sigma-Aldrich) were used as proxies to SOA. SOA particles were formed in the recently developed University of Vermont Environmental Chamber (UVMEC, 5.0 mil TeflonR FEP, Welch Fluorocarbon, Dover, NH) with a volume of 8 m³ operated in batch-mode. The Teflon UVMEC is equipped with separate gas and particle inlets, mixing fan, and filter sampling ports. A combined temperature/RH probe (Vaisala HMT331, Woburn, MA) is mounted on the interior of the chamber with all of the following experiments conducted indoors at room temperature. The α -pinene was introduced to the chamber by evaporating the required amount of hydrocarbon in a small flask held in a water

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bath through which a small flow rate of zero air was flushed into the chamber. After loading the hydrocarbon into the chamber, the formation of SOA was initiated by the addition of a short burst of ozone generated from dry, particle free air by a commercial high frequency corona discharge ozone generator (OL80A/DLS, OzoneLab, Burton, BC, Canada). The O_3 was quickly flushed into the chamber and simultaneously quantified with an ambient level monitor (Serinus O_3 Model E020010, American Ecotech, Cincinnati, OH). NO_x levels (as NO and NO_2) in the chamber were monitored with a commercial detector (EC9041A NO_x Analyser, American Ecotech, Cincinnati, OH) throughout the experiment, with concentrations less than 5 ppbv throughout these experiments.

SOA particle number and mass size distributions were measured as previously described for POA particles using the SMPS and CPC directly before introduction into the mass spectrometer through the particle inlet and lens system. In the following experiments polydisperse SOA particles were analyzed by NIR-LDI-AMS, with the mean diameter changing over the course of the experiment, and stated within the appropriate figure captions.

3 Results and discussion

3.1 Primary Organic Aerosols (POA)

The signal response of NIR-LDI-AMS for oleic acid (282 u) was monitored for the 281 m/z pseudo-molecular ion, $[OL-H]^-$, which was the base peak in the mass spectrum (Fig. 2, inset). A linear response was measured for $[OL-H]^-$ signal (S) as a function of POA mass deposited (M_{OL}). For these measurements, oleic acid aerosol mass loadings ranged from 0.15 to $4.4 \mu\text{g m}^{-3}$. Particles were deposited onto the LDI probe for variable times (5–30 s) to achieve total mass depositions in the range of 7 to 97 pg. The instrumental limit of detection (3σ) is calculated as 0.14 pg (or 140 fg), a significant improvement over existing soft ionisation methods for on-line, organic aerosol analysis,

such as PIAMS (Öktem et al., 2004), TD-PTRMS (Holzinger et al., 2010) and PERCI-AMS (LaFranchi and Petrucci, 2006) which was recently developed in our laboratory. The enhanced performance of NIR-LDI-AMS compared to that of PERCI-AMS likely is a result of the improved spatial and temporal overlap of the vaporization and ionization processes that is afforded by utilizing a single laser pulse.

For the case of oleic acid and other fatty acids, which often have elevated concentrations as high as 1 to 5 ng m⁻³ in urban environments (Fraser et al., 2002; Zheng et al., 2002; Robinson et al., 2006), ambient aerosol collection on the timescale of several minutes would be required to achieve this LOD. Since ambient loading of other low-volatility, oxygenated molecular markers common to urban aerosols, such as cholesterol and palmitoleic acid, often have atmospheric concentrations of the same order as oleic acid, our current research emphasis is on establishing the LOD of these and other species of atmospheric relevance. Initial measurements suggest an analytical performance analogous to that of oleic acid.

3.2 Secondary Organic Aerosols (SOA)

As proof of utility of the NIR-LDI-AMS to the measurement of atmospheric aerosols at ambient levels, SOA was generated by injection of 25 µL of α -pinene into the UVMEC, to achieve a mixing ratio of ~500 ppbv, and subsequent addition of a burst of ozone to an initial measured concentration of 750 ppbv. The ozone concentration decreased to 500 ppbv over the next hour (Fig. 3a), representing a pseudo steady state for O₃. SOA was sampled during this hour, while simultaneously monitoring the total organic mass concentration, C_{OA}. Notably, C_{OA} ranged from 1.6 to 12 µg m⁻³ for all measurements, which is within the reported range of total mass concentration of organic components of continental submicron aerosols (Cabada et al., 2004; Hock et al., 2008; Jimenez et al., 2009). Figures 3b-d show temporally correlated NIR-LDI mass spectral data from a typical α -pinene SOA experiment performed at these atmospherically relevant mass loadings.

The results obtained in this study highlight the utility of NIR-LDI-AMS for determining

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components of SOA in chamber-based experiments under conditions of atmospherically relevant mass concentrations of total particulate phase. The base peak in all trials in this and other experiments is 185 m/z , which is assigned to *cis*-pinic acid. The molecular structure of pinic acid and the other products measured are given in Table 1. A synthetic standard of *cis*-pinic acid was analyzed by NIR-LDI-AMS as deposited POA to support this assignment by insuring that this dicarboxylic acid did not extensively fragment in the desorption and ionization process. Another very strong ion signal in all collected spectra was 183 m/z , assigned to another major ozonolysis product of α -pinene, *cis*-pinonic acid. As noted by Hallquist et al. (2009) both *cis*-pinic acid and *cis*-pinonic acid are well established as major ozonolysis products of α -pinene and may also be produced from reactions of α -pinene with OH radical. Figure 4 shows the ion intensity, I_N , of *cis*-pinonic acid and other important products normalized to pinic acid (base peak). It should be noted that the assignment of the 183 m/z ion to *cis*-pinonic acid does not disallow for the contribution of other isomers to this ion signal. For example, possible contributors to the 183 m/z ion signal include the stereoisomers of OH-pinonaldehyde (184 u), which have been suggested products of α -pinene ozonolysis and contributors to SOA (Glasius et al., 2000; Iinuma et al., 2004; Camredon et al., 2010). The stereoisomers of OH-pinonaldehyde may arise from the gas-phase hydroxylation of pinonaldehyde (168 u) (Larsen et al., 2001), which was detected by NIR-LDI-AMS as a weak-to-medium intensity ion signal at 167 m/z . Furthermore, the strong 199 m/z ion signal suggests OH-radical initiated reactions with the 184 u product(s), giving 200 u (199 m/z) products that contain carboxyl moieties. The OH-radical initiated oxidation of OH-pinonaldehyde isomers (184 u) could give rise to 200 u products, namely the isomers of OH-pinonic acid (Table 2). OH-pinonic acid (i.e. hydroxypinonic acid) has been reported as a product in SOA derived from the ozonolysis of α -pinene (Yu et al., 1999; Gao et al., 2004; Tolocka et al., 2006; Camredon et al., 2010) and has been suggested to be a potential building block for higher molecular weight oligomers (Tolocka et al., 2006). Similarly the strong ion signal at 171 m/z ion is assigned to norpinic acid (172 u), which has been reported in other chamber-based studies (Yu et

al., 1999; Glasius et al., 2000; Camredon et al., 2010). This dicarboxylic acid may arise from a multiple step mechanism initiated by the OH oxidation of a dialdehyde. A logical candidate dialdehyde precursor to norpinic acid is 2,3-dimethyl-cyclobutane-1,3-dicarbaldehyde (140 u). The presence of this 140 u dialdehyde is supported by the moderate intensity 139 m/z ion signal in the NIR-LDI mass spectra. Other products shown in Table 2 include the 169 m/z ion that is assigned to pinalic and norpinonic acid (170 u), both of which having been reported in previous chamber studies (Yu et al., 1999; Glasius et al., 2000; Larsen et al., 2001), as well as a prominent unidentified product at 173 m/z .

4 Conclusions

This report has presented preliminary results for the analysis of organic aerosols by a new analytical technique with direct applicability to atmospheric science, namely: near-infrared laser desorption/ ionization aerosol mass spectrometry. This method has been shown to have single-compound limits of detection in the mid-to-low fg range, corresponding to total analysis times on the order of several minutes for SOA mass loadings on the order of a few $\mu\text{g m}^{-3}$. This detection limit represents an improvement of over two orders of magnitude from most other laser-driven “soft” ionization methods applied to AMS, such as VUV photoionization (Öktem et al., 2004) and PERCI-AMS (LaFranchi and Petrucci, 2006). A current effort is underway to assess the relative analytical figures of merit for NIR-LDI-AMS for a full-range of representative compounds common to ambient POA and SOA, including organic acids, high-molecular weight esters, and sterols.

The utility of NIR-LDI-AMS for chamber-based SOA formation studies was clearly demonstrated. The detection of important known SOA products arising from ozonolysis of α -pinene, including *cis*-pinic and *cis*-pinonic acid, at C_{OA} values from $<1 \mu\text{g m}^{-3}$ to $12 \mu\text{g m}^{-3}$ is within the reported range of total mass concentration of organic components of continental submicron aerosols (Cabada et al., 2004; Hock et al., 2008;

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Jimenez et al., 2009). The development and advancement of methods, such as NIR-LDI-AMS, will help the atmospheric research community simulate and measure SOA formation and growth under conditions that more closely represent the actual atmosphere. Ultimately, these advancements to atmospheric measurement techniques may help facilitate more accurate parameterizations of chamber-based SOA formation for modeling regional and SOA fluxes and aid in remediating the discrepancy between modeled and observed atmospheric total SOA production rates and concentrations.

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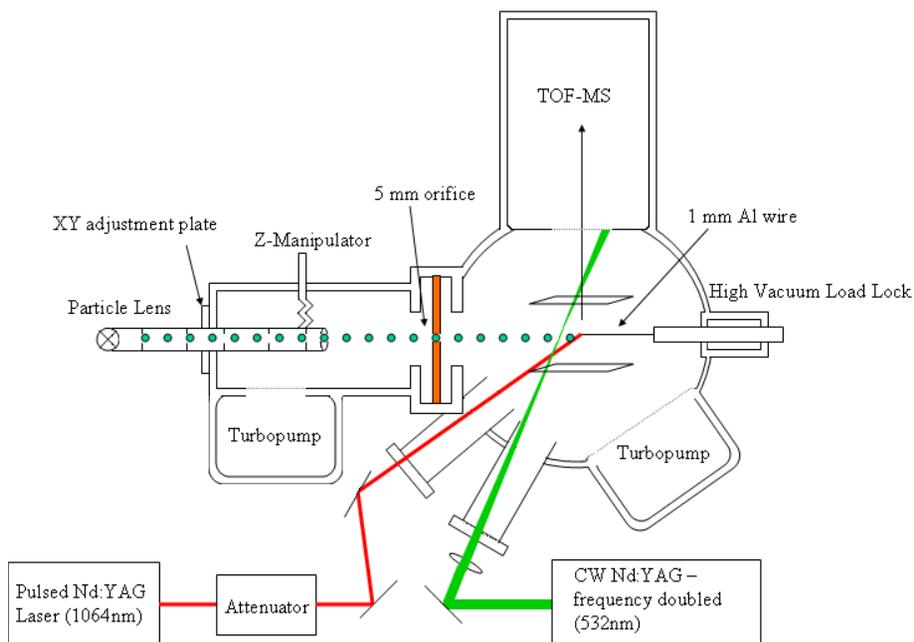
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Table 1. Particle-phase products of α -pinene ozonolysis measured by NIR-LDI-AMS as the $[M-H]^-$ pseudo-molecular ions. ^a Tentative assignment to one of several possible isomers (see text for further discussion).

2,3-dimethyl-cyclobutane-1,3-dicarbaldehyde	140 u	
Pinonaldehyde	168 u	
Pinalic acid	170 u	
Norpinonic acid	170 u	
Norpinic acid	172 u	
Cis-pinonic acid	184 u	
OH-pinonaldehyde ^a	184 u	
Pinic acid	186 u	
OH-pinonic acid ^a	200 u	

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**Fig. 1.** Schematic drawing of NIR-LDI-AMS.

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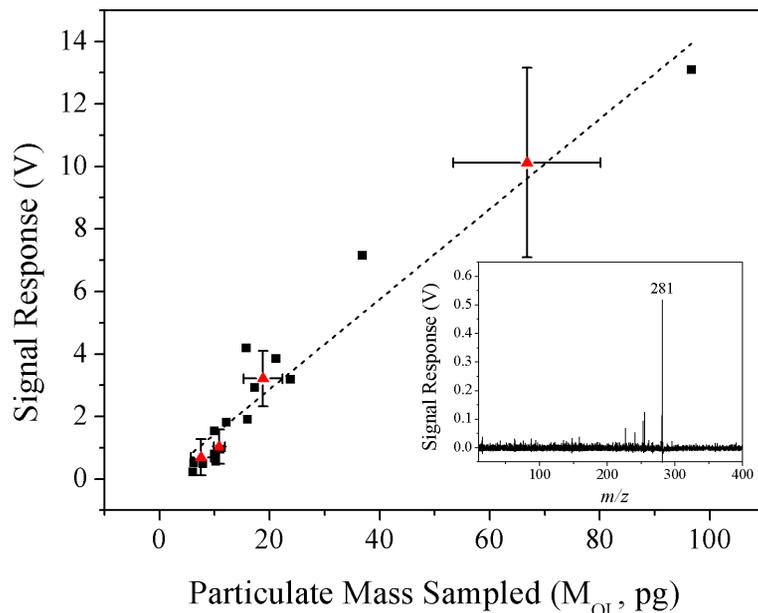


Fig. 2. Calibration curve for pure oleic acid particles (geometric mean diameter and standard deviation of 180 nm and 1.3, respectively). Equation of line is $S=0.144M_{OL} - 0.0113$; $R^2=0.923$. Black squares represent single measurements taken. Red triangles indicate averages for each sampling cluster. Inset: NIR-LDI-AMS spectrum of OL particles sampled from an aerosol with mass loading of $0.15 \mu\text{g m}^{-3}$ for 30 s (7.5 pg total mass sampled). Error bars represent 1 standard deviation.

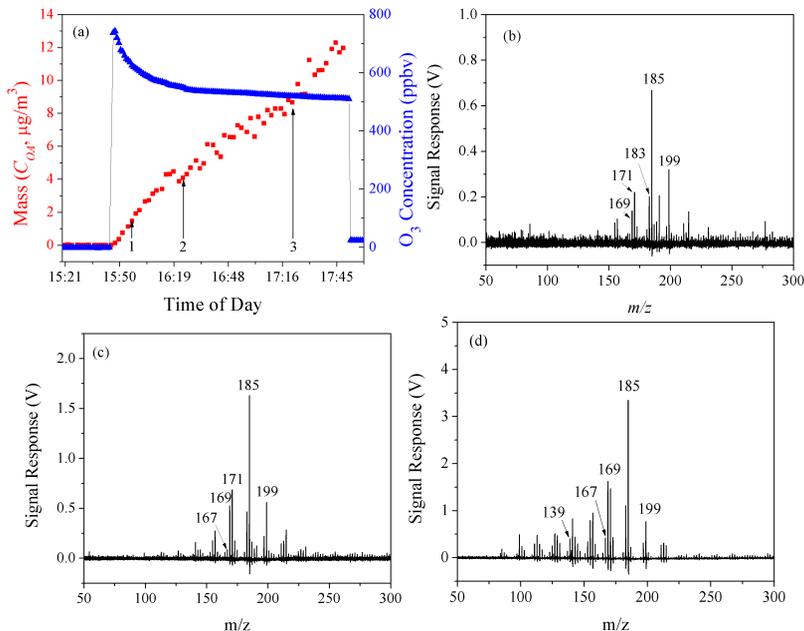


Fig. 3. Typical time-course data recorded during SOA formation in chamber from a-pinene ozonolysis, including **(a)** total aerosol mass loading (\blacksquare), C_{OA} , and ozone concentration (\blacktriangle) and NIR-LDI mass spectra at three different time points along the SOA growth curve: **(b)** Time point 1 with $C_{\text{OA}}=1.5 \mu\text{g m}^{-3}$; aerosol (number) geometric mean diameter of 132 nm and standard deviation of 1.31. **(c)** Time point 2 with $C_{\text{OA}}=4.1 \mu\text{g m}^{-3}$; aerosol (number) geometric mean diameter of 168 nm and standard deviation of 1.30. **(d)** Time point 3 with $C_{\text{OA}}=8.7 \mu\text{g m}^{-3}$; aerosol (number) geometric mean diameter of 197 nm and standard deviation of 1.30. Each mass spectrum is the result of a single, 2-min aerosol sampling into the NIR-LDI-AMS.

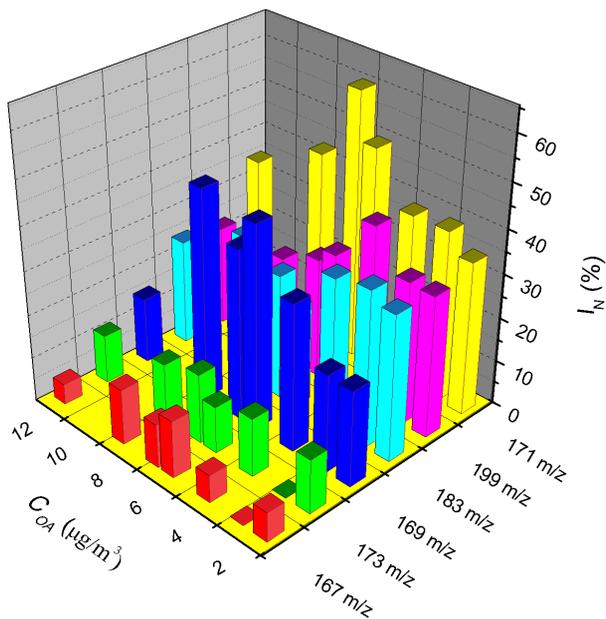


Fig. 4. Graph showing the intensity of various m/z peaks at evolving C_{OA} values as measured by NIR-LDI-AMS for the ozonolysis of α -pinene. See Fig. 3a for detailed particle mass concentrations and Table 1 for possible m/z assignments.