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Abstract

A single particle instrument has been developed for real-time analysis of organic aerosols. This instrument, named Single Particle Laser Ablation Mass Spectrometry (SPLAM), samples particles using an aerodynamic lens system for which the theoretical performances were calculated. At the outlet of this system, particle detection and sizing are realized using two continuous diode lasers operating at $\lambda = 403$ nm. Polystyrene Latex (PSL), sodium chloride (NaCl) and dioctylphthalate (DOP) particles were used to characterize and calibrate optical detection of SPLAM. The optical detection limit (DL) and detection efficiency (DE) were determined using size-selected DOP particles. The DE is ranging from 0.1 to 90 % for 100 and 350 nm DOP particles respectively and the SPLAM instrument is able to detect and size-resolve particles as small as 110–120 nm. Scattered light is detected by two photomultipliers and the detected signals are used to trigger a UV excimer laser ($\lambda = 248$ nm) used for laser desorption ionization (LDI) of individual aerosol particles. The formed ions are analyzed by a 1 m linear time-of-flight mass spectrometer in order to access to the chemical composition of individual particles. The TOF-MS detection limit for gaseous aromatic compounds was determined to be 0.85 attograms. DOP particles were also used to test the overall functioning of the instrument. The analysis of a secondary organic aerosol, formed in a smog chamber by the ozonolysis of indene, is presented as a first scientific application of the instrument. Single particle mass spectra are obtained with a global hit rate of 10 %. They are found to be very different from one particle to another, reflecting chemical differences of the analyzed particles, and most of the detected mass peaks are attributed to oxidized products of indene.

1 Introduction

Atmospheric aerosols are known to impact on human health (Vedal et al., 2006), atmospheric chemistry and climate (IPCC, 2007). These effects, which depend strongly

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on the aerosol's chemical composition, are still poorly understood. This is partly due to the incomplete characterization of the aerosol's chemical composition, in particular its organic fraction (Kanakidou et al., 2005).

Organic aerosols (OA) can be separated into primary organic aerosols (POA), directly emitted in the atmosphere, and secondary organic aerosols (SOA), formed by gas-to-particle conversion after atmospheric oxidation of anthropogenic and biogenic volatile organic compounds (VOC). Due to the large number of implicated molecules and to the diversity of their chemical functionalities and physico-chemical properties, the chemical composition of the organic fraction is complex. Moreover, complex processes such as SOA formation, cloud-aerosol interactions and atmospheric ageing remain poorly understood, partly because of the difficulty to describe the organic aerosol composition.

In this context, two main types of methods were adapted or developed to analyze OA and improve our knowledge of its composition and evolution. On the one hand, offline analytical techniques are used to elucidate these processes down to the molecular level. However, due to the complexity of the aerosol chemical composition, only a reduced fraction (up to 30 %) of the collected and extracted mass is identified on a molecular level (Cocker et al., 2001). Furthermore, these techniques are limited by a low temporal resolution because of the time needed to collect a sufficient amount of sample for analysis. On the other hand, real-time techniques (temporal resolution < 1 min), such as aerosol mass spectrometers (Sullivan and Prather, 2005), are also used to get a better understanding of the chemical processes, such as, for example SOA formation (Bahreini et al., 2005; Alfarra et al., 2006).

The ideal instrument as proposed by Jimenez et al. (2004) would meet all these requirements and allow for both a high temporal resolution and an access to the chemical speciation at the molecular level for each individual sampled particle. Due to their operating principle, aerosol mass spectrometers seem well suited to access to such analysis. They are generally composed by three operating parts: (1) a particle sampling interface, (2) an optical detection/sizing region, and (3) a mass spectrometer.

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A large number of techniques have been implemented in the development of aerosol mass spectrometers capable of determining the size, the morphology, the optical properties, or the elemental and molecular composition of particle in real time. Davis (1973) was the first to develop a thermal desorption aerosol mass spectrometer. In this instrument, aerosols are sampled through a steel capillary, impact on a heated surface (up to 1700 °C) and are flash-evaporated as an ionized gas that is then analyzed by a magnetic sector analyzer. Other surface ionization instruments were developed using quadrupole mass spectrometers (Lassiter and Moen, 1974; Myers and Fite, 1975) which are only capable of studying one m/z at a time. During the 1980's, this one-step vaporization/ionization technique has evolved to become a two-step technique by coupling a flash vaporization, at lower temperatures, to electron impact ionization of the vaporized species (Allen and Gould, 1981; Sinha et al., 1982). Nowadays, the commercially available Aerodyne Aerosol Mass Spectrometer (AMS) still uses this scheme (Jayne et al., 2000; Drewnick et al., 2005; Canagaratna et al., 2007). In the same way, Tobias and Ziemann (1999) used a Temperature-Programmed Thermal Desorption Particle Beam Mass Spectrometry (TDPBMS) to achieve successive vaporization of components according to their vapor pressures such as for SOA formed in a smog chamber (Tobias et al., 2000). Thereafter, Atmospheric Pressure Chemical Ionization Mass Spectrometry (APCI-MS) (Hoffmann et al., 2002) has been used as a soft ionization technique, compared to electron impact, and several m/z could be scanned at a time using an ion trap mass spectrometer.

Knowing that thermal desorption allows analyzing many particles simultaneously, the development of laser aerosol mass spectrometry techniques was an opportunity to obtain single particle information in real time (Prather et al., 1994; Weiss et al., 1997). Aerosols, focused into the mass spectrometer for example by an aerodynamic lens system (ALS), are detected by one or two continuous wave (cw) lasers. They are perpendicularly crossed to the particle beam and are mostly operated in the visible spectral range. In the case of two detection lasers, particles can be aerodynamically sized by measuring their travel time between both laser beams. The measured particle

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velocity can then be used easily to calculate the necessary time delay to trigger a pulsed laser (IR or UV) for individual particle desorption and ionization. The formed ions are then detected by mass spectrometry. This kind of technique is able to give physical and chemical properties of individual particles in real time. It was firstly introduced by Sinha (1984), who used Nd:YAG laser pulses at 266 nm for the particle desorption/ionization step and a quadrupole mass spectrometer for the chemical analysis. Other laser-based single particle mass spectrometers were developed later by the Prather group (Prather et al., 1994; Nordmeyer and Prather, 1994; Noble et al., 1994).

The real power of this technique came up by combining the laser desorption/ionization (LDI) step with Time-of-Flight mass spectrometry (TOF-MS) for ion analysis (McKeown et al., 1991). Because of its pulsed mode of operation, TOF-MS is ideally suited to be linked to a pulsed desorption/ionization method. Note that only the power density (in $W m^{-2}$) of a nanosecond laser pulse is high enough to provide substantial and rapid desorption of molecules from solid material. Other advantages of TOF-MS are its ability to obtain an entire mass spectrum on the order of microseconds, the theoretical unlimited mass range and its ion transmission efficiency close to 100 %, independent of mass. Several groups designed such single particle instruments and they have been used to address a large variety of scientific cases (Hinz et al., 1994; Murphy and Thomson, 1995; Carson et al., 1995; Reents et al., 1995; Noble and Prather, 1996; Weiss et al., 1997; Gard et al., 1997; Murphy et al., 1998; Woods et al., 2001; Hunt and Petrucci, 2002). Besides the simultaneous sizing and chemical composition analysis, real time single particle techniques are able to provide information for each sampled particle.

One short-coming of the LDI technique is the fragmentation of organic molecules since the number of photons absorbed by a specific molecule during the LDI process cannot be efficiently controlled and thus dissociative ionization is not avoidable. Molecular speciation is difficult to achieve in these conditions. However, we note that interesting results relevant for the investigation of OA chemistry, as for example the

identification of oligomeric species or the chemical characterization of different types of SOA, can nevertheless be obtained with an LDI instrument (Gross et al., 2006; Huang et al., 2007).

One way to overcome the fragmentation problem is to use Two-Step Laser Desorption/Ionization (L2DI) where vaporization and ionization are separated in time by a few microseconds. The first vaporization step can be achieved without ionizing the parent molecules which permits to reduce the UV laser power density for the second step in order to ionize molecular species near their ionization thresholds by, for example, Resonant-Two Photon Ionization (R2PI) or Single Photon Ionization (SPI) with VUV laser radiation or synchrotron radiation. Single particle L2DI was investigated by the T. Baer and K. Prather groups in the early 2000's who successfully studied micrometer sized droplets consisting of pure substances (Morrical et al., 1998; Cabalo et al., 2000; Woods et al., 2001; Smith et al., 2002). Single-particle L2DI was also used successfully to identify molecular tracers of different type of real-world traffic-related and wood combustion aerosols such as polycyclic aromatic hydrocarbons (Bente et al., 2008, 2009). These results have shown that single particle L2DI can be achieved yielding fragment-free mass spectra. However, it is still a real analytical challenge to adapt and apply this technique for an exhaustive investigation of the chemical analysis of OA particles containing a complex mixture of species that easily undergo dissociative ionization.

In this paper, we present a newly built real-time single-particle aerosol mass spectrometer, named "SPLAM" for Single-Particle Laser Ablation Mass Spectrometry. This LDI-based instrument has been developed in our laboratory to sample, detect, determine the size and analyze organic *single* particle in real time. The development and characterization of the ALS, the optical detection system, the TOF-MS, and the triggering process are outlined. As a first application, we present results obtained for the analysis of a SOA produced in the laboratory from ozonolysis of indene in CESAM simulation chamber in LISA (Wang et al., 2011).

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2 System design

The SPLAM instrument is composed of three main parts (Fig. 1): (1) an aerodynamic focusing lens system to sample and introduce the particles into the vacuum system by forming a beam of very low divergence, and two differentially pumping stages; (2) the optical detection/aerodynamic particle sizing region which permits the determination of the aerodynamic diameter of the detected particles and the synchronization with the third part of the instrument and; (3) the chemical characterization region which consists of a vaporization/ionization region and a linear time-of-flight mass spectrometer with 1 m field free drift region. The TOF-MS with its aerosol inlet is very compact and mounted on a scientific table with rolls. It can thus be moved easily. This table is mechanically separated from the laser sources of SPLAM which are all placed on an additional 1.2 × 2.2 m optical table (Newport). Each part of the instrument is presented in the next sections.

2.1 The aerodynamic lens system

Aerosol mass spectrometry relies on the capability to bring particles into a high vacuum system and to focus them spatially into the ion source of a mass spectrometer. For this purpose, the aerodynamic lens system developed initially in Peter McMurry's group (Liu et al., 1995a,b) has been widely used by many groups and for many different applications. Concerning the SPLAM instrument, a new ALS was designed using the theoretical model and operational software described by Wang et al. (2005a,b, 2006). The following criteria have been considered: (1) transmission of a broad diameter range (100 to 2000 nm) corresponding to the size range of atmospheric aerosol containing the highest organic fraction (Zhang et al., 2007), (2) good transmission efficiency with low beam divergence, and (3) acceleration of particles to a specific speed in function of their diameters (100 to 150 m s⁻¹).

Our lens system has been exactly machined according to the dimensions calculated by Wang's design tool (1/10 mm precision for orifices, 1/100 mm precision for

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the alignment). A technical drawing in real scale is presented in Fig. 2. Our ALS is composed of five orifices mounted in a precision stainless steel tube and starting from 6.93 mm at the inlet and gradually decreasing to 3.11 mm at the exit, all separated by 90 mm spacers. Note that these orifices can be exchanged if different lens prop-
 5 erti μm critical orifice (Microcontrol) into the aerodynamic lens. The volume flowrate has been measured to be $0,083 \text{ l min}^{-1}$, in good agreement with the model calculations. Downstream this orifice, a relaxation chamber limits the perturbations caused by the sampling process. The first four lenses focus the particles onto a centre line and the final exit aperture – the accelerating nozzle – controls gas expansion and particle ac-
 10 celeration into the vacuum system. This 7 mm diameter final nozzle plays an important role for the particle beam diameter determination (Liu et al., 1995a,b). The outlet of the lens system is located in the first vacuum chamber where a 250 l s^{-1} turbomolecular pump (Varian, model V301) is used to maintain a pressure of 10^{-3} mbar when the lens inlet is open (10^{-7} mbar with closed ALS).

Wang's design tool (Wang et al., 2006) also allows to model the theoretical perfor-
 15 mances for an ALS of given dimensions. For our system, a theoretical transmission efficiency of 100 % was calculated for particle diameters ranging from 200 nm up to $4 \mu\text{m}$ and more than 90 % for particles diameter larger than 30 nm. Downstream the accelerating nozzle, the theoretical particle beam diameter is calculated to be smaller
 20 than 1 mm up to the ion source of the TOF-MS (20 cm downstream the accelerating nozzle).

The ALS is fixed and can only be moved in the direction of particle traveling. The fo-
 25 cused particles continue to travel along a straight-line path towards the detection/sizing chamber by passing successively through two pinholes. These pinholes have respec- tively inner diameters of 1.5 and 1 mm and a length of 5 and 23 mm. When the lens inlet is open, the small vacuum chamber between the two pinholes – its extension is 2 cm – is maintained at 10^{-4} mbar using a 68 l s^{-1} turbomolecular pump (Varian, model V70).

2.2 The optical detection/aerodynamic particle sizing region

The real-time sizing of a particle and the synchronization between its detection and its ionization and mass analysis remains a major challenge in aerosol mass spectrometry. One way to provide improved size information is achieved by incorporating a two-laser particle velocity measurement as implemented in the SPLAM instrument.

2.2.1 Description of the optical detection

After exiting the first two differential pumping stages, the particles enter into the optical detection/sizing region ($P = 10^{-5}$ mbar when ALS inlet is open) where they pass through two continuous wave (cw) diode laser beams emitting light at $\lambda = 403$ nm (Coherent Radius, $P \approx 40$ mW). This wavelength has been chosen in order to enhance the detection efficiency for particles of $d < 500$ nm. At the same time, being at the edge of the visible spectral range, the violet light still permits a relatively easy alignment of the two lasers.

These cw laser beams are spaced by 41 ± 0.5 mm and respectively called L1 and L2 (Figs. 1 and 3). Outside the vacuum system, an optical spatial filter and a beam collimation system are used for both laser beams to respectively limit the stray light and optimize the intersection of the particle and the laser beam (not shown). The Gaussian shaped cross sections of the laser beams have been determined experimentally at the intersection zone using a CCD camera (Gentec, "Beam'R"). They are 315.5 and 334.8 μm at $1/e^2$ and 760.9 and 755.4 μm at 1.5% for L1 and L2 respectively with experimental powers of $P_{L1} = 41.3$ mW and $P_{L2} = 31.2$ mW.

Figure 3 is a technical drawing with the real scale. When a particle passes through each laser beam, its scattered light is detected by two photomultipliers (PMT, Photonis, XP2930). These PMTs, separated by glass windows from the vacuum system, have circular active areas of 23 mm diameter and are placed at an angle of 34° with respect to the forward direction of the laser beams. The PMT active areas are placed at a 37 mm distance from the intersection between particle and laser beams, which defines

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a detection angle of $34 \pm 13^\circ$. According to Mie theory, the maximum of scattered light is in the forward direction, independent of wavelength. However, as can be seen in Fig. 3, mechanical constraints do not permit to set the PMT closer to the laser beam in our configuration.

To limit the stray light inside the detection chamber and thus the noise on the PMT, the internal walls were completely blackened and two sets of four diaphragms were inserted inside of both laser inlets (Fig. 3) which efficiently avoid penetration of reflected light from the entrance windows. Finally, two light horns are used to trap the photons at both laser exits (not shown in Fig. 3).

2.2.2 Aerodynamic particle sizing: description and calibration

When particles pass through the first laser beam, the scattered light generates a signal to the first PMT which triggers an external timing circuit which has been programmed on a field programmable gate array (FPGA, see Sect. 2.4.). The passage in the second laser beam allows for particle velocity determination by measuring the transit time (t_{opt}) of the particle between two laser beams for the given beam separation (41 ± 0.5 mm). Vacuum aerodynamic diameters (d_{aev}), defined as the diameter of a sphere with standard density which has the same terminal velocity as the particle of interest (DeCarlo et al., 2004), are then derived for three types of size selected aerosols, as shown in Fig. 4. This figure shows experimental calibration curves for aerodynamic particle sizing measurements performed with four certified sizes of PolyStyrene Latex (PSL, Duke Scientific Corp.), and selected DioctylPhthalate (DOP) and sodium chloride (NaCl) particle diameters using a differential mobility analyzer (DMA, model 3080L, TSI inc.). These particles were produced using an atomizer (model 3076, TSI inc.) and a diffusion dryer (model 3062, TSI inc.) to remove water in the case of PSL and NaCl particle generation. Each point represents the average of hundred detected particles and the horizontal error bars correspond to an error propagation of 95% confidence intervals. In order to avoid the detection of two or more particles at the same time during these experiments, the number concentration of the aerosol to

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is given for DOP particles whereas the SPLAT (Zelenyuk et al., 2005) (open squares) and ATOFMS (Su et al., 2004) (open diamonds) DEs are given for PSL particles.

A close-up of panel a from 50 to 250 nm is shown in panel b. From panel b, the optical detection limit of SPLAM can be estimated to be at about 100 nm particle aerodynamic diameter (DE = 0.4 %). As expected, close to the detection limit, the DE is relatively poor (below 5 %). However, it increases rapidly towards bigger particles reaching a maximum of 74 % at 350 nm.

The SPLAT and ATOFMS DEs are very similar to those obtained for SPLAM, although in these two instruments elliptical mirrors for the collection of scattered photons are implemented in order to enhance their DEs. One way to understand the similar DEs obtained for fine particles despite fairly different optical setups is to consider the differences in the cw laser wavelengths used. In fact, the ATOFMS and SPLAT both operate with green cw lasers ($\lambda = 532$ nm) whereas the violet laser implemented inside SPLAM favors the detection of fine and ultrafine particles according to Mie theory. However, the decrease towards the 1 μm is somewhat more pronounced in our instrument as compared to SPLAT which could also be a difference due to different wavelengths used.

2.3 Chemical characterization region: the photoionization time-of-flight mass spectrometer

After being detected and sized, the particles enter the ionization source of the mass spectrometer where short-lived burst of ions are produced. Time-of-flight mass analyzers are ideally suited for characterizing simultaneously all the ions formed during the LDI process for each detected particle.

An home-made TOF mass spectrometer was implemented in the SPLAM instrument. After passing through a 1 mm orifice with a length of 5 mm, the particles reach the TOF-MS ionization region where a pressure of 10^{-8} mbar is maintained by two 250 l s^{-1} turbomolecular pumps (Varian V301). The pressure in this region does not change at all when the ALS inlet is opened. This is particularly important since it means that our

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differential pumping system is very efficient and that our TOF-MS will *exclusively* detect compounds from the aerosol phase. This has been further evidenced by introducing gaseous toluene via the ALS inlet. R2PI ($\lambda = 248$ nm) coupled to TOF-MS is extremely sensitive to aromatic hydrocarbons (see also below). No toluene could be detected under these conditions.

A 17 mJ excimer laser (KrF, Optex, LambdaPhysik) emitting at $\lambda = 248$ nm was used as a desorption/ionization laser at a maximum repetition rate of 10 Hz and a pulse width of 10 ns. The laser is focused into the ion source by an $f = 30$ cm fused silica lens. The ion extraction region of the TOF-MS is slightly off-focus yielding a 7.5×1 mm rectangular shaped spot size in this region which is horizontally oriented in order to optimize the mass resolution and to maximize the hit efficiency since particles will travel through the longer axis of this rectangle. Here, the laser power density reaches about 1.4×10^7 W cm⁻² (at 12 mJ pulse energy).

The TOF-MS itself is of linear configuration and is operating according to the Wiley-McLaren ion space focusing conditions (Wiley, McLaren, 1955). It has a two-stage accelerating electric field consisting of a three copper plate grids, spaced by 1 cm. The length of the field free drift region is 1 m. A Behlke high voltage switch (HTS 21-06-GSM) is used to extract the ions orthogonally to the particle beam. The Behlke switch has a very steep edge (<3 ns) and thus favors good mass resolution. Moreover, in order to further improve the mass resolution, a delay time τ is applied for the ion extraction (see Sect. 2.4) (Wiley and McLaren, 1955). The acceleration potentials used are +145 and -1460 V respectively for the extraction and acceleration region. Positive ions are detected by two 40 mm microchannel plate detectors in series (MCP, Hamamatsu). The signals are preamplified (Ortec fast preamplifier) and sent to an acquisition card (National Instruments, PXI-5621, 64 MHz, 14 bit vertical resolution) interfaced to a personal computer. In its latest version, the TOF-MS achieves a mass resolution of $m/\Delta m \approx 500$ (for LDI desorbed DOP molecules).

The sensibility of the TOF-MS has been characterized using an effusive inlet for gaseous molecules, coupled directly to the ion source chamber. Using the KrF excimer

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$\lambda = 248$ nm for Resonance-Enhanced Multiphoton-Ionization (REMPI) will be a method well suited for the detection of particle-bound aromatic molecules, such as for example those found in anthropogenic or biomass burning aerosols. This conclusion will be emphasized in Sect. 3.2 by the study of the chemical composition of SOA formed by the ozonolysis of indene as first scientific application of SPLAM.

2.4 Synchronization of optical detection and LDI mass spectrometry

The synchronization between the optical detection and the desorption/ionization laser is achieved using a Field Programmable Gate Array card (FPGA, Avnet, ADSADS-XLX-V4FX-EVL12-G). Figure 6 shows the chronogram of this process. The trigger time t_{trig} is calculated from the residence time t_{opt} of the particles between both continuous lasers. Since the trigger delay (i.e. the temporal separation between an external pulse and emission of photons) of the excimer laser is 450 ± 5 ns, this additional time delay has to be taken into account to exactly synchronize the impact of the UV photons to an arriving particle. Considering their measured particle velocities and the associated uncertainties, particles are expected to arrive in a 1.86×1 mm area, homogeneous in energy, in the middle of the 7.5×1 mm laser spot (see Sect. 2.3). Moreover, as already mentioned in the Sect. 2.3, a delay time of $2.55 \mu\text{s}$ is applied before extracting the produced ions in order to enhance mass resolution.

In the single particle mode of operation, the maximum analysis rate is 10 particles per second since at a higher repetition rate, the decrease of the excimer laser pulse energy is too important. Therefore, an upper limit of 10 Hz was programmed for the laser pulse repetition rate. In its current state, the synchronization of the SPLAM instrument allows the laser triggering from t_{opt} determination. However, at this stage of development, the time t_{opt} associated with the mass spectrum of the sampled particle is not recorded.

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3 First results

As explained before, the SPLAM instrument was designed to study the organic fraction of atmospheric aerosol particles. The study of SOA produced in one of the LISA simulation chamber CESAM was performed as the first scientific application of SPLAM.

5 Prior to this study, some preliminary test experiments were performed using DOP particles in order to test the overall functioning of the instrument.

3.1 Preliminary tests using DOP particles

In order to test the feasibility of the synchronization procedure between the optical detection and the vaporization/ionization region of the SPLAM instrument, preliminary tests were performed using DOP (Sigma Aldrich, >99 % purity) particles generated by nebulization of the pure viscous oil using a constant output atomizer (TSI, model 3076).

3.1.1 Characterization of blank level

Figure 7a shows a typical noise level on the mass spectra obtained for a single laser pulse on a filtered N₂ flux. The maximum and minimum thresholds of an ion signal to be considered as significant were calculated as three times the standard deviation obtained at each mass. These levels are presented as red shaded area on the panel A and a 4 mV threshold was then determined for the whole spectra by excluding the higher noise located around *m/z* 25.

3.1.2 Mass spectra of individual DOP particles

20 Figure 7b shows a typical mass spectrum of an individual DOP particle. For this experiment, the produced particle concentration was diluted by a factor of 1000. The laser power density was $1 \times 10^8 \text{ W cm}^{-2}$ with a 1 mm^3 ionization volume.

We mention that every single particle mass spectrum was repeatable in terms of peak position indicating that the TOF time scale is constant. As mentioned before, in

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the amount of internal energy released to the parent cation is not far from to the one transferred during the EI process. However, there is one striking difference: in the EI-MS of DOP, m/z 279 is a strong ion (25 % relative to the base peak m/z 49) whereas this peak is absent in the single particle LDI mass spectra. It is known from work comparing 70 eV EI ionization to photoionization using tunable VUV synchrotron radiation (Schwell et al., 2000) that during the 70 eV EI process, approximately 20 eV of the 70 eV electron kinetic energy is transferred as internal energy to the molecule. It can thus be concluded that at least 4 photons of 248 nm (5 eV) are transferred to the DOP neutral molecules during LDI, and probably a little more since m/z 279 is apparently also fragmented during LDI.

3.1.3 Particle hit rate determination of SPLAM

The hit rate, which is defined as the ratio between the numbers of particles hit by the vaporization/ionization laser that generate ions detectable by the mass spectrometer, and the number of particles sized by the optical detection during the same time period, was determined to be 15 % in these preliminary experiments. This corresponds to a typical hit rate obtained by other single particle aerosol mass spectrometers (Su et al., 2004). Unfortunately, approximately half of the single particle mass spectra exhibit very intense and unidentifiable broad mass peaks, appearing between m/z 40 and m/z 65 (not shown). This is explained as an ion extraction artifact inside the ion source of the TOF-MS. In these cases, the LDI ion plume is probably formed at the edge of the extraction region which does not allow proper extraction and space focalization of the ions. Therefore, these spectra have to be discarded and the effective hit rate, corresponding to the fraction of *analyzable* mass spectra, is thus estimated to be about 7–8 %.

We can conclude from these preliminary experiments using DOP particles that all three parts of our instrument – (1) sampling a polydisperse aerosol using the aerodynamic lens system, (2) particles sizing by a two-fold optical detection, and (3) synchronization with LDI and measurement of single particles mass spectra by TOF-MS

– work properly. The instrument is thus adapted for single particle analysis of organic aerosols. In order to scientifically validate the SPLAM instrument, we have analyzed a SOA formed in smog chamber experiment and main results are described in the following section.

3.2 Study of aromatic SOA produced from indene ozonolysis

3.2.1 SOA production and sampling in the CESAM chamber

Aromatic SOA were produced in the CESAM simulation chamber described elsewhere (Wang et al., 2011). A brief description is given here: the 4.2 m³ stainless steel chamber is equipped by a pumping system to deeply clean the chamber between experiments and to limit wall memory effects. An internal fan allows for homogeneous mixing of gaseous species and aerosols. In the case of our indene ozonolysis study, the chamber was filled with 80 % N₂ (U quality, Air Liquide) and 20 % O₂ (Alphagaz 1, Air Liquide) after several pumping cycles. A 1 ppm concentration of ozone, produced by an UV lamp, was injected and controlled using an ozone analyzer (Horiba model APOA-370). The volatile precursor, indene (Sigma Aldrich, 99 % purity), was then injected to yield a 1 ppm concentration. This aromatic precursor was chosen for its known high potential to form secondary organic aerosols (Chiappini, 2006). The temporal evolution of the size distribution of produced particles during this experiment was monitored using a Scanning Mobility Particle Sizer (TSI, DMA model 3080 + CPC model 3010) and is presented in Fig. 8. Between the beginning and the end of this experiment, the mean diameter of the measured size distribution was shifted from 80 to 100 nm with maximum number concentrations of 4×10^3 to 1×10^3 particles cm⁻³ respectively. As for DOP experiment, a separated aerodynamic sizing of the detected SOA particles during this experiment, using the optical detection of the SPLAM instrument, allowed to determine the sampled d_{aev} range being comprised between 170 and 900 nm which correspond to the bigger particles formed inside the chamber, i.e. the extreme right part of the distribution, which is consistent knowing the optical SPLAM DL.

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3.2.2 Characterization of the blank level

The CESAM chamber was connected to SPLAM via a 4 mm inner diameter copper tube. The length of this tube was kept as short as possible (about 1.5 m). Figure 9, lowest panel, shows the typical noise level of the SPLAM mass spectrum obtained for a single laser pulse when gas was sampled (SPLAM aerosol inlet open, CESAM chamber filled with synthetic air and ozone, but without indene). The red shaded area, presented on this panel, was calculated as three times the standard deviation obtained at each mass and corresponds to the maximum and minimum thresholds of an ion signal to be considered as significant. From this calculation, the maximum level was determined to be 4 mV. This level is also indicated as red shaded area in Fig. 10a and b.

3.2.3 Single particle mass spectra and SOA chemical composition analysis

During this five hour aerosol formation experiment, single particle mass spectra were obtained about two hours after the ozone injection, with a global hit rate of about 10 % (see Sect. 3.1.3). The mass spectra were subdivided into two groups taking into account the type of observed mass peaks and their signal intensity.

Figure 9a–c shows representative single particle mass spectra corresponding to a first group. About 80 % of the analyzable mass spectra belong to this group which is characterized by three relatively intense fragments, at m/z 39, 57 and 63. These fragments are assigned to organic cations formed by dissociative ionization of larger hydrocarbons (HC). For example, m/z 63 ($C_5H_3^+$) is a typical fragment observed in the ionic fragmentation of aromatic HC which in turn makes sense considering the chemical system under study. On the contrary, m/z 39 ($C_3H_3^+$) and m/z 57 ($C_4H_9^+$) are generally weak in the EI-MS fragmentation of aromatic HC. These two fragments are considered to be typical in the MS of aliphatic HC or molecules with aliphatic side chains. However, since LDI apparently transfers a little more internal energy to the molecules

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the moment. They might belong to cations formed by ionization of other non-identified products or even of organic oligomers which could be present in the indene SOA.

3.2.4 Discussion of the first results of SPLAM

Even though during the LDI process dissociative ionization of the molecules present in the aerosol phase is predominant, the SPLAM instrument has detected high molecular weight ions originating from indene degradation products in the particulate phase. This can be seen as a step forward compared to SOA analysis studies involving the AMS instrument from Aerodyne (Bahreini et al., 2005; Alfarra et al., 2006). Indeed, the main studies involving this instrument for chemical analysis of SOA give rise to a very high fragmentation level and common dominant fragments at m/z 41, 43, 44 and 55 are observed in all mass spectra. This does not permit to lead a real chemical mechanism investigation at the molecular level.

The SPLAM instrument configuration is very similar to the one developed by Huang et al. (2007) who also measured single particle LDI mass spectra. These authors investigated SOA formation initiated by OH photooxidation of five aromatic hydrocarbons: benzene, toluene, ethylbenzene, p-xylene, and 1,2,4 trimethylbenzene. To our knowledge, this is the only smog chamber study of anthropogenic type SOA, formed from aromatic HC, and using LDI single particle mass spectrometry for analysis. Huang et al. analyzed a few hundred mass spectra for each of the five types of SOA and determined an appearance frequency distribution for the eight main mass peaks (m/z 18, 29, 43, 44, 46, 57, 67, 77). For all five types of SOA, m/z 57 is by far the most abundant mass peak. On the contrary, m/z 39 and 63 which are observed in our group 1 mass spectra (80% of all MS in our study) are much less frequent in the experiments of Huang et al. It is interesting to note that these authors also observe many high molecular weight ions (up to m/z 186) despite the fragmentation induced by LDI. However, these ions seem to be less abundant since they do not appear in their appearance frequency analysis. This is qualitatively in accordance with our results since only 20% of our single particle MS show ions with higher m/z ratios. The study of Huang et

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al. (2007) confirms that fragmentation induced by LDI seems to be less problematic compared to a thermal desorption AMS, at least for the analysis of SOA formed by aromatic precursors.

4 Conclusions

5 A single particle aerosol mass spectrometer, called SPLAM (Single Particle Laser Ab-
lation Mass Spectrometry), equipped with an aerodynamic lens system, a two-fold opti-
cal detection and a 1 m linear TOF-MS, has been developed, calibrated and char-
acterized. The instrument was designed to detect and analyze sub-micrometer sized
organic aerosol particles. The transmission of the aerodynamic lens system has been
10 modeled and designed using the program developed by Wang et al. (2006). The lens
transmits particles with diameters comprised between 200 nm and 4 μm with a the-
oretical efficiency of 100 % into a beam of very low divergence (diameter < 1 mm at
the ion source). The optical detection limit in terms of particle size was determined
to be at 100 nm approximately. The two-fold optical detection efficiency DE is mea-
15 sured to be 0.4 % at $d_{\text{aev}} = 10$ nm and 74 % at $d_{\text{aev}} = 350$ nm. After aerodynamic sizing,
the particles enter the TOF-MS which is equipped with an excimer laser emitting at
 $\lambda = 248$ nm used for one step particle laser desorption/ionization (LDI). The mass reso-
lution is $m/\Delta m = 500$. The laser is triggered by the optical particle detection upstream.
The three stage differential pumping of SPLAM excludes any detection of gas phase
20 compounds.

The instrument has been fully characterized and scientifically validated by a study
of SOA produced in a smog chamber from ozonolysis of indene. The obtained mass
spectra were classified in two groups with a 10 % global hit rate. The first group, which
represents 80 % of the total mass spectra number, is characterized by three relatively
25 intense fragments at m/z 39, 57 and 63 while a second group additionally presents
fragments with higher m/z , up to 280 and represents 20 % of the total mass spectra.

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Group 2 mass spectra are very different from one to another and we think that this reflects different chemical types of particles to be present in the indene SOA. However, under LDI conditions different particle sizes could give different fragmentation patterns of the aerosol phase compounds as has been pointed out. This issue has to be investigated in more detail in the future.

Our results have been compared to those of Huang et al. (2007) who recently studied SOA formed from gaseous aromatic precursors, using LDI single particle TOF-MS. They are qualitatively consistent with our work since similar types of mass spectra are observed (see Sect. 3.2.4).

The lack of reference spectra adapted for LDI conditions has so far hindered molecular speciation. Also, more statistics are needed to measure the frequency of occurrence of ions, including those with high molecular weight. This kind of data could then help to measure more significant fragment ion intensity ratios to be compared to the adapted reference spectra. This is crucial for molecular speciation under LDI conditions.

Different experimental approaches are also possible to proceed towards molecular speciation with SPLAM, for example the use of L2DI or SPI. Both techniques permit to ionize molecules close to their ionization threshold and therefore reduce the number of dissociative ionization reactions. Molecular speciation is probably more straightforward in these conditions since fewer mass peaks will appear per molecule. As an example, SPI using synchrotron radiation, coupled to flash vaporization on a heated surface, has been used recently with success to chemically analyze ensemble of nanoparticles (Mysak et al., 2005; Wilson et al., 2006; Gloaguen et al., 2006; Gaie-Levrel et al., 2011).

More generally, it has to be noted also that signal to noise ratios in single particle mass spectrometry of nanometer sized *and* chemically complex particles are very low, even when very sensitive detection techniques are used. A statistic evaluation, over at least a few hundreds of particles, is necessary to understand the real chemical meaning of the mass spectra. The real-time character of this type of measurements is then somewhat reduced. For example, if a few hundred particles are needed for chemical

analysis, the maximum time resolution would be a few minutes with the current particle analysis rate.

We note that a statistical evaluation – like the frequency of occurrence analysis of ions – does not obstruct the single particle information. Rather, it is way to analyze a large number of low intensity mass spectra. Different chemical sub-groups of single particle MS could still be identified in parallel.

Finally, we can conclude that the SPLAM instrument shows a high potential to study SOA from aromatic precursors using LDI, especially once a statistical evaluation over a few hundred particles will be implemented. For other types of SOA, formed from non-aromatic precursors, other experimental approaches like L2DI or SPI are necessary. Combustion aerosols could also be a scientific target of SPLAM since PAH are present for which very low detection limits have been measured. Finally, all type of aromatic pollutants present in the aerosol phase and their atmospheric dynamics could be measured with SPLAM in real time.

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- Alfarra, M. R., Paulsen, D., Gysel, M., Garforth, A. A., Dommen, J., Prévôt, A. S. H., Worsnop, D. R., Baltensperger, U., and Coe, H.: A mass spectrometric study of secondary organic aerosols formed from the photooxidation of anthropogenic and biogenic precursors in a reaction chamber, *Atmos. Chem. Phys.*, 6, 5279–5293, doi:10.5194/acp-6-5279-2006, 2006.
- Allen, J. and Gould, R. K.: Mass spectrometric analyzer for individual aerosol particles, *Rev. Sci. Instrum.*, 52, 804–809, 1981.
- Bahreini, R., Keywood, M. D., Ng, N. L., Varutbangkul, V., Gao, S., Flagan, R. C., Seinfeld, J. H., Worsnop, D. R., and Jimenez, J. L.: Measurements of Secondary Organic Aerosol from Oxidation of Cycloalkenes, Terpenes, and m-Xylene Using an Aerodyne Aerosol Mass Spectrometer, *Environ. Sci. Technol.*, 39, 5674–5688, 2005.
- Bente, M., Sklorz, M., Streibel, T., and Zimmermann, R.: Online Laser Desorption-Multiphoton Postionization Mass Spectrometry of Individual Aerosol Particles: Molecular Source Indicators for Particles Emitted from Different Traffic-Related and Wood Combustion Sources, *Anal. Chem.*, 80, 8991–9004, 2008.
- Bente, M., Sklorz, M., Streibel, T., and Zimmermann, R.: Thermal Desorption-Multiphoton Ionization Time-of-Flight Mass Spectrometry of Individual Aerosol Particles: A Simplified Approach for Online Single-Particle Analysis of Polycyclic Aromatic Hydrocarbons and Their Derivatives, *Anal. Chem.*, 81, 2525–2536, 2009.
- Cabalo, J., Zelenyuk, A., Baer, T., and Miller, R. E.: Two-Color Laser Induced Evaporation Dynamics of Liquid Aerosols Probed by Time-of-Flight Mass Spectrometry, *Aerosol Sci. Tech.*, 33, 3–19, 2000.
- Canagaratna, M. R., Jayne, J. T., Jimenez, J. L., Allan, J. D., Alfarra, M. R., Zhang, Q., Onasch, T. B., Drewnick, F., Coe, H., Middlebrook, A., Delia, A., Williams, L. R., Trimborn, A. M., Northway, M. J., DeCarlo, P. F., Kolb, C. E., Davidovits, P., and Worsnop, D. R.: Chemical and microphysical characterization of ambient aerosols with the Aerodyne aerosol mass spectrometer, *Mass Spectrom. Rev.*, 26, 185–222, 2007.
- Carson, P. G., Neubauer, K. R., Johnston, M. V., and Wexler, A. S.: Online Chemical-Analysis of Aerosols by Rapid Single-Particle Mass-Spectrometry, *J. Aerosol Sci.*, 26, 535–545, 1995.
- Chiappini, L.: Développement d'une technique d'analyse pour l'étude de la composition chimique et des voies de formation de l'aérosol organique secondaire en atmosphère simulée, PhD Thesis, University Paris Diderot-Paris 7, 2006.

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- Chiappini, L., Perraudin, E., Durand-Jolibois R., Doussin, J.-F., Development of a supercritical fluid extraction – gas chromatography – mass spectrometry method for the identification of highly polar compounds in secondary organic aerosols formed from biogenic hydrocarbons in smog chamber experiments, *Anal. Bioanal. Chem.*, 386, 1749–1759, 2006.
- 5 Chung, S. H. and Seinfeld, J. H.: Global distribution and climate forcing of carbonaceous aerosols, *J. Geophys. Res.*, 107(D19), 4407–4440, 2002.
- Cocker III, D. R., Mader, B. T., Kalberer, M., Flagan, R. C., and Seinfeld, J. H.: The effect of water on gas–particle partitioning of secondary organic aerosol: II. m-xylene and 1,3,5-trimethylbenzene photooxidation systems, *Atmos. Environ.*, 35, 6073–6085, 2001.
- 10 Davis, W. D.: Surface ionization mass spectroscopy of airborne particulates, *J. Vac. Sci. Technol.*, 10, 278, 1973.
- DeCarlo, P. F., Slowik, J. G., Worsnop, D. R., Davidovits, P., and Jimenez, J. L.: Particle morphology and density characterization by combined mobility and aerodynamic diameter measurements, Part 1: Theory, *Aerosol Sci. Tech.*, 38, 1185–1205, 2004.
- 15 Drewnick, F., Hings, S. S., DeCarlo, P., Jayne, J. T., Gonin, M., Fuhrer, K., Weimer, S., Jimenez, J. L., Demerjian, K. L., Borrmann, S., and Worsnop, D. R.: A New Time-of-Flight Aerosol Mass Spectrometer (TOF-AMS) – Instrument Description and First Field Deployment, *Aerosol Sci. Tech.*, 39, 637–658, 2005.
- Gaie-Levrel, F.: Ph.D. thesis, Université Paris Diderot, Paris, 7, 2009.
- 20 Gaie-Levrel, F., Gutlé, C., Jochims, H.-W., Rühl, E., Schwell, M.: Photoionization of Atmospheric Aerosol Constituents and Precursors in the 7–15 eV Energy Region: Experimental and Theoretical Study, *J. Phys. Chem. A*, 112, 5138–5151, 2008.
- Gaie-Levrel, F., Schwell, M., Garcia, G., and Nahon, L.: VUV state-selected photoionization of thermally-desorbed biomolecules by coupling an aerosol source to an imaging photoelectron/photoion coincidence spectrometer: case of the amino-acids tryptophan and phenylalanine, *Phys. Chem. Chem. Phys.*, 13, 7024–7036, 2011.
- 25 Gard, E., Mayer, J. E., Morrical, B. D., Dienes, T., Ferguson, D. P., and Prather, K.: Real-time analysis of individual atmospheric aerosol particles: Design and performance of a portable ATOFMS, *Anal. Chem.*, 69, 4083–4091, 1997.
- 30 Gloaguen, E., Mysak, E., Leone, S. R., Ahmed, M., and Wilson, K. R.: Investigating the chemical composition of mixed organic-inorganic particles by “soft” vacuum ultraviolet photoionization: the reaction of ozone with anthracene on sodium chloride particles, *Int. J. Mass Spectrom.*, 258, 74–85, 2006.

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Gross, D. S., Gälli, M. E., Kalberer, M., Prevot, A. S. H., Dommen, J., Alfarra, M. R., Duplissy, J., Gaeggeler, K., Gascho, A., Metzger, A., and Baltensperger, U.: Real time measurement of oligomeric species in secondary organic aerosol with the aerosol time-of-flight mass spectrometer, *Anal. Chem.*, 78, 2130–2137, 2006.

5 Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, Th. F., Monod, A., Prévôt, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, *Atmos. Chem. Phys.*, 9, 5155–5236, doi:10.5194/acp-9-5155-2009, 2009.

Hinz, K. P., Kaufmann, R., and Spengler, B.: Laser-Induced Mass Analysis of Single Particles in the Airborne State, *Anal. Chem.*, 66, 2071–2076, 1994.

15 Hoffmann, T., Bandur, R., Hoffmann, S., and Warscheid, B.: On-Line Characterization of Gaseous and Particulate Organic Analytes Using Atmospheric Pressure Chemical Ionization Mass Spectrometry, *Spectrochim. Acta B*, 57, 1635–1647, 2002.

Huang, M., Zhang, W., Hao, L., Wang, Z., Zhao, W., Gu, X., Guo, X., Liu, X., Long, B., and Fang, L.: Laser desorption/ionization mass spectrometric study of secondary organic aerosol formed from the photooxidation of aromatics, *J. Atmos. Chem.*, 58, 237–252, 2007.

20 Hunt, A. L. and Petrucci, G. A.: Analysis of ultrafine and organic particles by aerosol mass spectrometry, *Trac-Trends Anal. Chem.*, 21, 74–81, 2002.

IPCC – International Panel on Climate Change: Changes in Atmospheric constituents and in radiative forcing, In: *Climate Change 2007: The Physical Science Basis*, Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, edited by: Forster, P., Ramaswamy, V., Artaxo, P., Berntsen, T., Betts, R., Fahey, D. W., Haywood, J., Lean, J., Lowe, D. C., Myhre, G., Nganga, J., Prinn, R., Raga, G., Schulz, M., and Van Dorland, R., Cambridge University Press, Cambridge, 2007.

25 Jayne, J. T., Leard, D. C., Zhang, X. F., Davidovits, P., Smith, K. A., Kolb, C. E., and Worsnop, D. R.: Development of an Aerosol Mass Spectrometer for Size and Composition Analysis of Submicron Particles, *Aerosol Sci. Tech.*, 33, 49–70, 2000.

30 Jimenez, J. L.: Aerosol Mass Spectrometry Part 2: Thermal desorption techniques, American association for aerosol research (AAAR), Annual Conference, Atlanta, GA, 2004.

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- Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C. J., Swietlicki, E., Putaud, J. P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G. K., Winterhalter, R., Myhre, C. E. L., Tsigaridis, K., Vignati, E., Stephanou, E. G., and Wilson, J.: Organic aerosol and global climate modelling: a review, *Atmos. Chem. Phys.*, 5, 1053–1123, doi:10.5194/acp-5-1053-2005, 2005.
- Lassiter, W. S. and Moen, A. L.: In situ mass analysis of particles by surface-ionization mass spectrometry, NASA Technical Memorandum X-3112, 1–15, 1974.
- Liu, P., Ziemann, P. J., Kittelson, D. B., and McMurry, P. H.: Generating Particle Beams of Controlled Dimensions and Divergence: I. Theory of Particle Motion in Aerodynamic Lenses and Nozzle Expansions, *Aerosol Sci. Tech.*, 22, 293–313, 1995a.
- Liu, P., Ziemann, P. J., Kittelson, D. B., and McMurry, P. H.: Generating Particle Beams of Controlled Dimensions and Divergence: II. Experimental Evaluation of Particle Motion in Aerodynamic Lenses and Nozzle Expansions, *Aerosol Sci. Tech.*, 22, 314–324, 1995b.
- McKeown, P. J., Johnston, M. V., and Murphy, D. M.: Online Single-Particle Analysis by Laser Desorption Mass-Spectrometry, *Anal. Chem.*, 63, 2069–2073, 1991.
- Morriscal, B. D., Fergenson, D. P., and Prather, K. A.: Coupling two-Step laser desorption/ionization with aerosol time-of-flight mass spectrometry for the analysis of individual organic particles, *J. Am. Soc. Mass Spectrom.*, 9, 1068–1073, 1998.
- Mühlberger, F., Wieser, J., Ulrich, A., and Zimmermann, R.: Single photon ionization (SPI) via incoherent VUV-Excimer light: Robust and compact Time-of-flight mass spectrometer for on-line, real-time process gas analysis, *Anal. Chem.*, 74, 3790–3801, 2002.
- Mühlberger, F., Wieser, J., Ulrich, A., and Zimmermann, R.: Single photon ionization mass spectrometry with a novel electron-pumped excimer lamp for detection of trace compounds from thermal processes, *Organohalogen Compd.*, 66, 795–799, 2004.
- Murphy, D. M. and Thomson, D. S.: Laser Ionization Mass-Spectroscopy of Single Aerosol Particles, *Aerosol Sci. Tech.*, 22, 237–249, 1995.
- Murphy, D. M., Thomson, D. S., and Mahoney, M. J.: In Situ Measurements of Organics, Meteoritic Material, Mercury, and Other Elements in Aerosols at 5 to 19 Kilometers, *Science*, 282, 1664–1669, 1998.
- Myers, R. L. and Fite, W. L.: Electrical detection of airborne particulates using surface ionization techniques, *Environ. Sci. Technol.*, 9, 334–336, 1975.

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- Su, Y., Sipin, M. F., Furutani, H., and Prather, K. A.: Development and Characterization of an Aerosol Time-of-Flight Mass Spectrometer with Increased Detection Efficiency, *Anal. Chem.*, 76, 712–719, 2004.
- Suess, D. T. and Prather, K. A.: Mass spectrometry of aerosols, *Chem. Rev.*, 99, 3007–3035, 1999.
- Sullivan, R. C. and Prather, K. A.: Recent Advances in Our Understanding of Atmospheric Chemistry and Climate Made Possible by On-Line Aerosol Analysis Instrumentation, *Anal. Chem.*, 77, 3861–3886, 2005.
- Sykes, D. C., Woods III, E., Smith, G. D., Baer, T., and Miller, R. E.: Thermal vaporization-vacuum Ultraviolet Laser Ionization Time-of-Flight Mass Spectrometry, *Anal. Chem.*, 74, 2048–2052, 2002.
- Tobias, H. J. and Ziemann, P. J.: Compound Identification in Organic Aerosols Using Temperature- Programmed Thermal Desorption Particle Beam Mass Spectrometry, *Anal. Chem.*, 71, 3428–3435, 1999.
- Tobias, H. J., Kooiman, P. M., Docherty, K. S., and Ziemann, P. J.: Real-Time Chemical Analysis of Organic Aerosols Using a Thermal Desorption Particle Beam Mass Spectrometer, *Aerosol Sci. Tech.*, 33, 170–190, 2000.
- Tsigaridis, K. and Kanakidou, M.: Global modelling of secondary organic aerosol in the troposphere: a sensitivity analysis, *Atmos. Chem. Phys.*, 3, 1849–1869, doi:10.5194/acp-3-1849-2003, 2003.
- Vedal, S. and Dutton, S. J.: Wildfire air pollution and daily mortality in a large urban area, *Environ. Res.*, 102, 29–35, 2006.
- Wang, J., Doussin, J.-F., Perrier, S., Perraudin, E., Katrib, Y., Pangu, E., and Picquet-Varrault, B.: Design of a new multi-phase experimental simulation chamber for atmospheric photo-smog, aerosol and cloud chemistry research, *Atmos. Meas. Tech. Discuss.*, 4, 315–384, doi:10.5194/amtd-4-315-2011, 2011.
- Wang, X. and McMurry, P. H.: A Design Tool for Aerodynamic Lens Systems, *Aerosol Sci. Tech.* 40, 320–334, 2006.
- Wang, X., Kruis, F. E., and McMurry, P. H.: Aerodynamic focusing of nanoparticles: I. Guidelines for Designing aerodynamic lenses for nanoparticles, *Aerosol Sci. Tech.*, 39, 611–623, 2005a.

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Wang, X., Gidwani, A., Girshick, S. L., and McMurry, P. H.: Aerodynamic focusing of nanoparticles: II. Numerical simulation of particle motion through aerodynamic lenses, *Aerosol Sci. Tech.*, 39, 624–636, 2005b.

Weiss, M., Verheijen, P. J. T., Marijnissen, J. C. M., and Scarlett, B.: On the performance of an on-line time-of-flight mass spectrometer for aerosols, *J. Aerosol Sci.*, 28, 159–171, 1997.

Wiley, W. C. and McLaren, I. H.: Time-of-Flight mass spectrometer with improved resolution, *Rev. Sci. Instrum.*, 26, 1150–1157, 1955.

Wilson, K. R., Jimenez-Cruz, M., Nicolas, C., Belau, L., Leone, S. R., and Ahmed, M.: Thermal Vaporization of Biological Nanoparticles: Fragment-Free Vacuum Ultraviolet Photoionization Mass Spectra of Tryptophan, Phenylalanine Glycine Glycine, and β -Carotene, *J. Phys. Chem. A*, 110, 2106–2113, 2006.

Woods, E., Smith, G. D., Dessiaterik, Y., Baer, T., and Miller, R. E.: Quantitative detection of aromatic compounds in single particle mass spectrometry, *Anal. Chem.*, 73, 2317–2322, 2001.

Zelenyuk, A. and Imre, D.: Single Particle Laser Ablation Time-of-Flight Mass Spectrometer: An Introduction to SPLAT, *Aerosol Sci. Tech.*, 39, 554–568, 2005.

Zhang, Q., Jimenez, J. L., Canagaratna, M. R., Allan, J. D., Coe, H., Ulbrich, I., Alfarra, M. R., Takami, A., Middlebrook, A. M., Sun, Y. L., Dzepina, K., Dunlea, E., Docherty, K., DeCarlo, P. F., Salcedo, D., Onasch, T., Jayne, J. T., Miyoshi, T., Shimonono, A., Hatakeyama, S., Takegawa, N., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Williams, P., Bower, K., Bahreini, R., Cottrell, L., Griffin, R. J., Rautiainen, J., Sun, J. Y., Zhang, Y. M., and Worsnop, D. R.: Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically influenced Northern Hemisphere midlatitudes, *Geophys. Res. Lett.*, 34, L13801/1–L13801/6, 2007.

Zimmermann, R., Heger, H. J., Kettrup, A., and Boesl, U.: A mobile resonance laser ionization time-of-flight mass spectrometry – Device for on-line analysis of aromatic pollutants in waste incinerator flue gases, *Rapid Commun. Mass Sp.*, 11, 1095–1102, 1997.

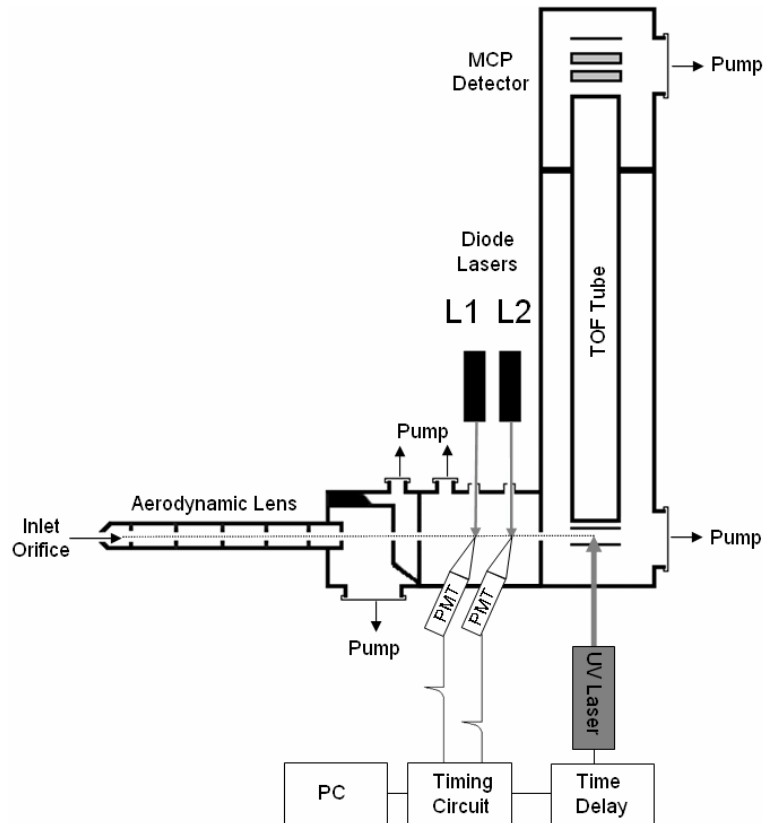


Fig. 1. Schematic illustration of the Single Particle Laser Ablation Mass Spectrometry (SPLAM) instrument. Particles are focused by an aerodynamic lens system. The particle beam crosses two continuous diode laser beams allowing optical detection of individual particles and determination of their respective aerodynamic diameter. An external timing circuit permits to trigger a UV laser to vaporize and ionize individual particles. The formed ions are analyzed by the time-of-flight mass spectrometer.

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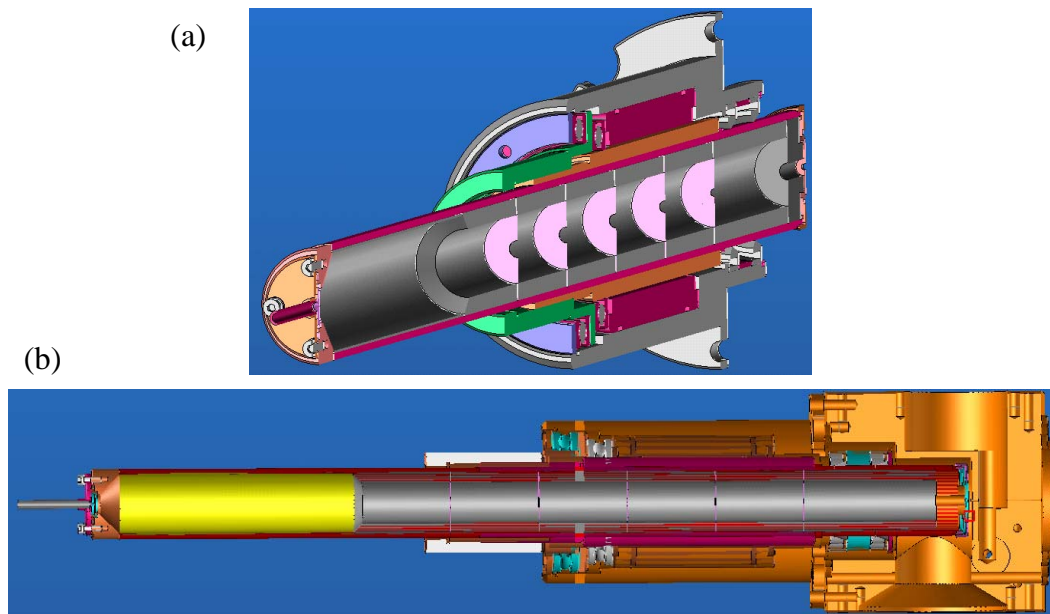


Fig. 2. Scheme of the aerodynamic lens system of SPLAM and its z-translation mechanism (vertical cuts). **(a)** View of the five lens orifices and the relaxation chamber. **(b)** View of the ALS integrated into the first two pumping stage regions (drawings: Mecaconcept).

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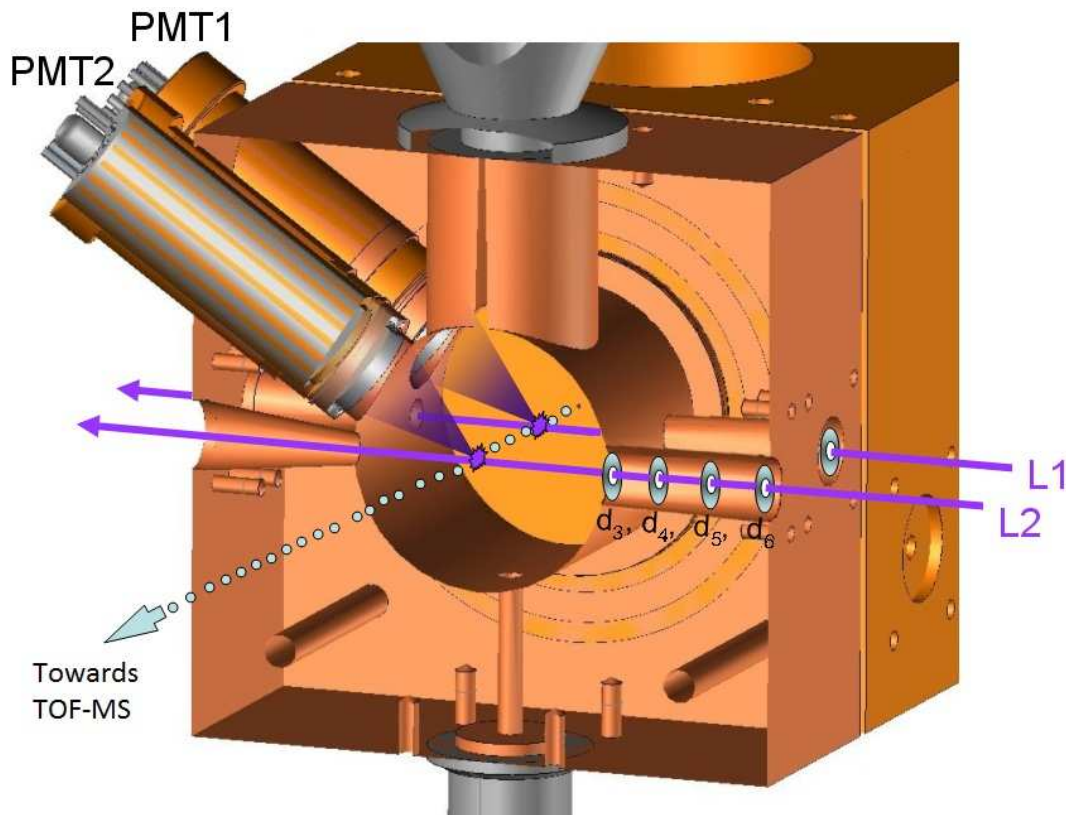


Fig. 3. Optical detection chamber of SPLAM. The particle beam crosses two diode laser beams (L1 and L2). Scattered light is detected in forward direction by two photomultiplier tubes at an angle of $34 \pm 13^\circ$ (centre of active detection area, see Sect. 2.2). The four diaphragms inserted into the tunnels of the incoming laser light avoid the penetration of reflected light from the entrance windows (not shown) into the detection chamber. The laser beams are trapped by light horns (not shown).

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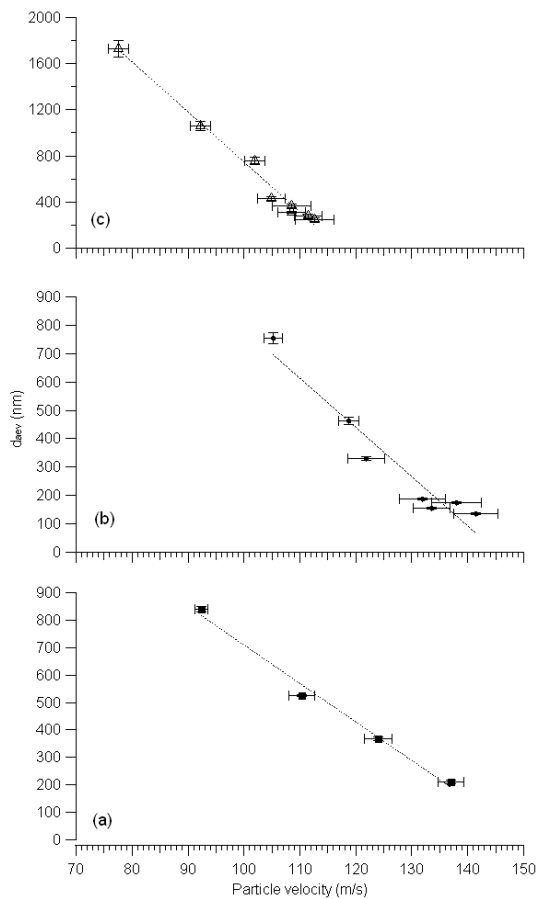


Fig. 4. Experimental calibration curves for aerodynamic particle sizing of the SPLAM instrument obtained for (a) PSL, (b) DOP and (c) NaCl particles. The dash lines correspond to linear guideline.

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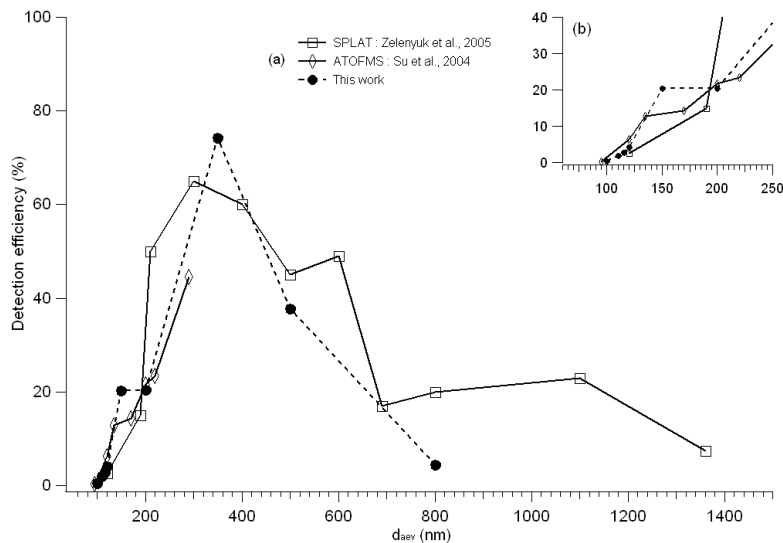
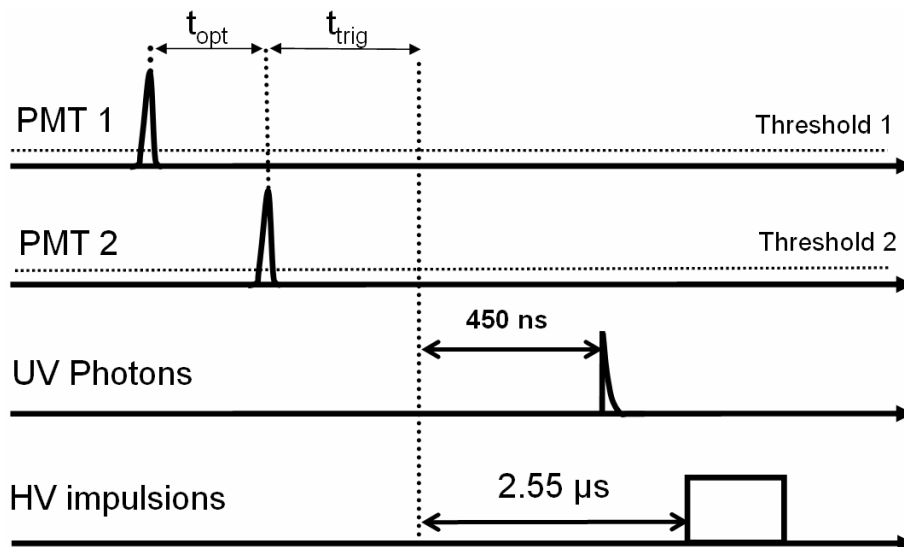


Fig. 5. (a) DOP particles detection efficiency for SPLAM instrument (black circles) and PSL particles detection efficiency for SPLAT (Zelenyuk et al., 2005) (open squares) and ATOFMS (Su et al., 2004) (open diamond) instruments plotted as a function of vacuum aerodynamic diameter, (b) close up of the graph (a) between 50 and 250 nm.

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**Fig. 6.** Chronogram of the synchronization between optical detection and laser triggering.[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

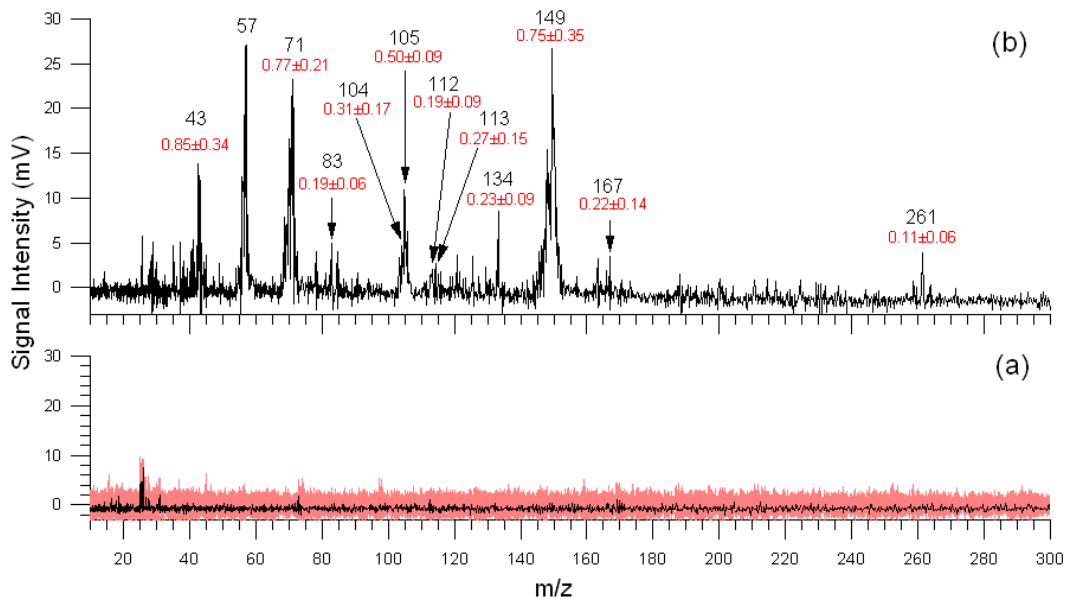


Fig. 7. (a) Typical noise level on the mass spectra obtained for a single laser pulse when aerodynamic lens system has sampled a filtered N_2 flux. The red shaded area, calculated as three times the standard deviation obtained at each mass, corresponds to the maximum and minimum thresholds of an ion signal to be considered as significant, (b) typical mass spectrum of an individual DOP particle. The mean intensity ratios of each detected mass peak normalized to m/z 57 and their associated standard deviation are indicated below the mass peaks identifications.

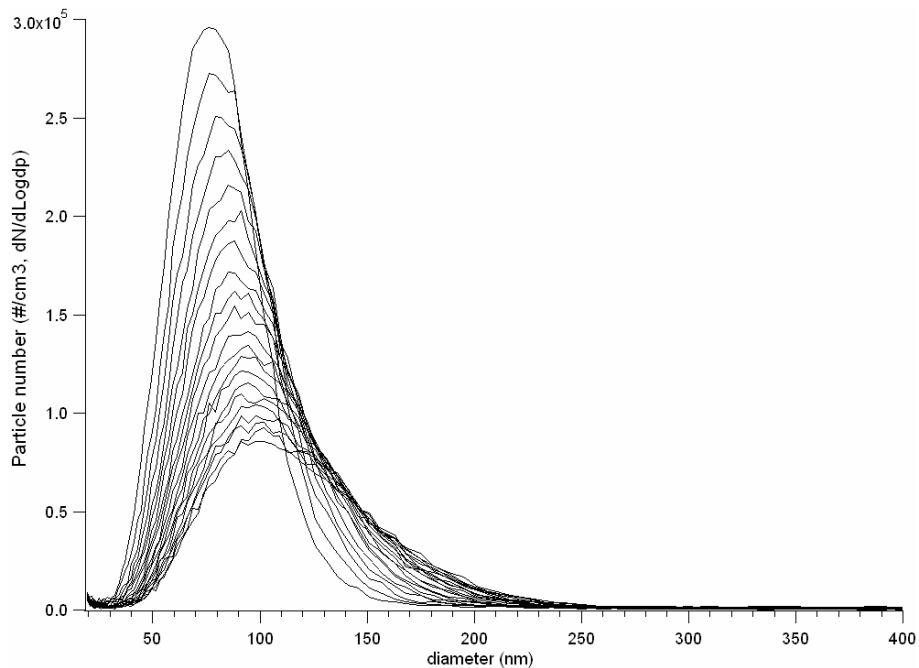


Fig. 8. Temporal evolution of the size distribution of produced SOA.

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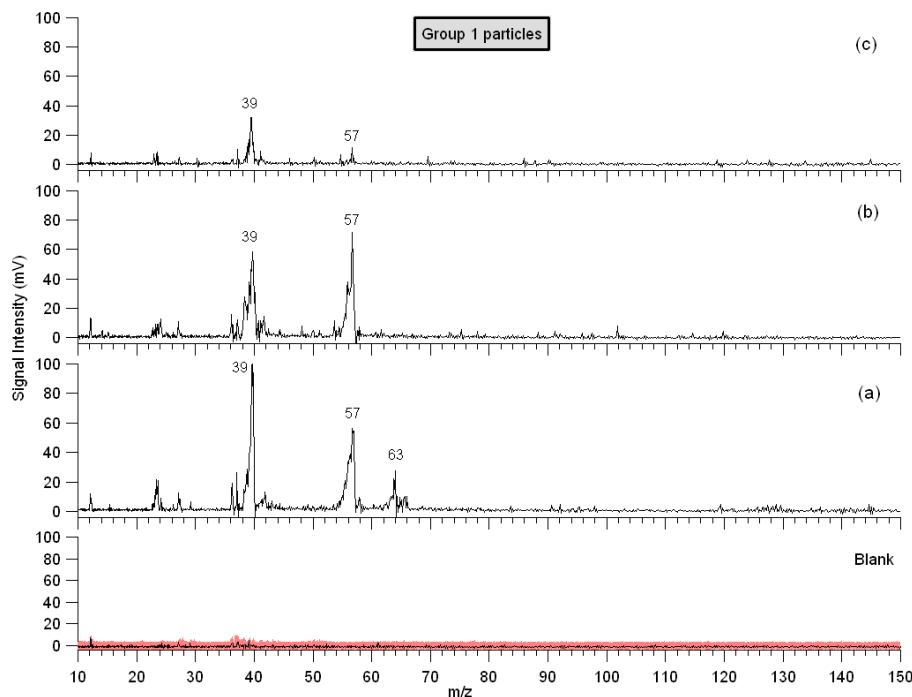


Fig. 9. Blank: typical noise level on the mass spectra obtained for a single laser pulse (SPLAM inlet open, CESAM chamber, filled with synthetic air and ozone, but without indene). The blank level is determined to be at 4 mV (indicated as red shaded zone). See text for further explanations; **(a)**, **(b)**, **(c)**: examples of a single particle mass spectra of SOA produced by ozonolysis of indene in the smog chamber CESAM (group 1 particles).

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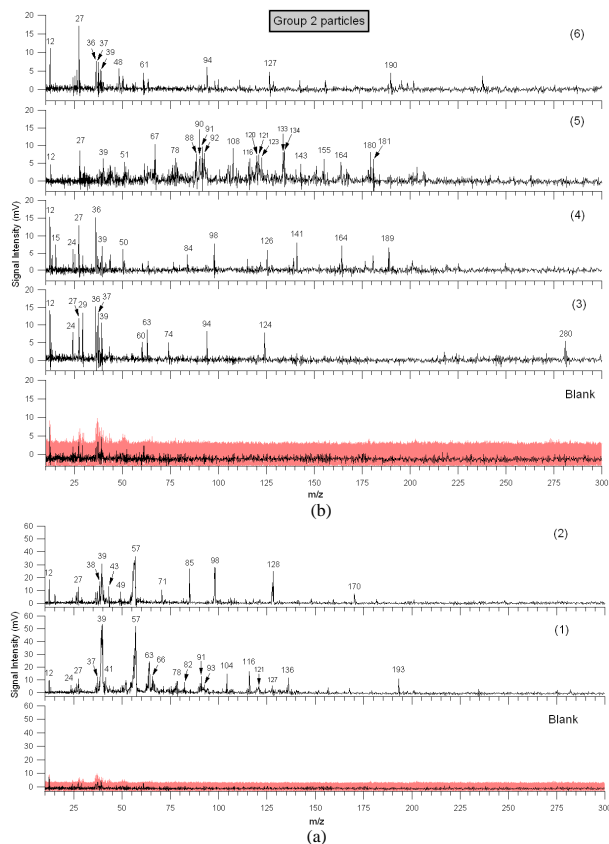


Fig. 10. Single particle mass spectra of SOA produced by ozonolysis of indene in the smog chamber CESAM (group 2 particles). **(a)** and **(b)** have different ordinate scaling. The blank level is determined to be at 4 mV (indicated as red shaded zone in the lowest panels). See text for further explanations.

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