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An on-line aerosol laser mass spectrometer with three, easily interchangeable laser based ionisation methods for characterisation of inorganic and aromatic compounds on particles

M. Bente[a], T. Adam[a,b], T. Ferge[a,1], S. Gallavardin[a,2],
M. Sklorz[a,b], T. Streibel[a,b], R. Zimmermann[a,b,c,*]

[a] GSF-Forschungszentrum für Umwelt und Gesundheit, Institut für Ökologische Chemie, 85764 Neuherberg, Germany
[b] Universität Augsburg, Institut für Physik, Analytische Chemie, 86159 Augsburg, Germany
[c] BIfA-Bayerisches Institut für Angewandte Umweltforschung und technik GmbH, Abteilung Umwelt und Prozesschemie, 86167 Augsburg, Germany

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Abstract

An aerosol mass spectrometric set-up is presented comprising three different laser based techniques for on-line analysis of particles. The implemented methods are one-step laser desorption/ionisation (LDI), two-step laser desorption/photoionisation (LDPI) and thermal desorption/photoionisation (TDPI). Photoionisation processes for the latter two methods are based on resonance enhanced multiphoton ionisation (REMPI), which is highly selective and sensitive for polyaromatic hydrocarbons (PAH). LDI is especially suitable for the detection of inorganic compounds and the determination of sum values such as elemental carbon content. Investigated samples were particles from spruce wood ash generated by an oxygen-controlled residential heating system and exhaust gases from a gasoline driven passenger car. In the positive LDI mass spectra several metal cations such as potassium and iron are detectable, whereas carbon clusters can be observed with the negative mode. With LD-REMPI and TD-REMPI various PAH such as phenanthrene and derivatives, pyrene, etc., become visible. In the wood ash samples relatively high yields of retene were found, which could be used as tracer compound for coniferous wood combustion. All three modes can be applied with only slight modifications of the instrument. Thus, it allows characterising single particles on a real time basis and, depending on the application, the most convenient technique can be selected.

Keywords: ATOFMS; Thermal desorption; REMPI; PAH; Retene

1. Introduction

Numerous epidemiological studies report on the correlation of elevated levels of particulate matter (PM) in ambient air and adverse human health effects [1–18]. Fine particles (Ø < 2.5 μm) are of special concern due to their high surface-to-volume ratio and their ability to penetrate deeply into the lungs [19–21]. Toxicological tests on animals and in situ experiments showed that both physical and chemical properties of the particles are involved in toxic, genotoxic and carcinogenic health effects [22–24]. A significant contribution of organic constituents to the observed health effects is likely and a particular important compound class in this context are the polycyclic aromatic hydrocarbons (PAH). This compound class comprehends a large number of species many of them being highly toxic and carcinogenic. PAH may be involved in long-term health effects such as carcinogenesis, oxygenated PAH are suspected to play a role in the induction of oxidative stress [25,26]. The latter is currently discussed as a possible explanation for the association of PM exposure and pulmonary or cardiovascular short-term health effects. Important PAH sources to the atmosphere include motor vehicles [27–30], power generation via combustion of coal and oil [27,31–33], incineration [27,31] and wood burning [34–37].

Regarding the analysis of collected PM mostly conventional off-line techniques, such as gas chromatography–mass

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[*] Corresponding author. Tel.: +49 89 3187 4544; fax: +49 89 3187 3510.
E-mail address: ralf.zimmermann@gsf.de (R. Zimmermann).

[1] Present address: British American Tobacco (Germany) GmbH, Weiherstr. 26, 95448 Bayreuth, Germany.

[2] Present address: ETH Zürich, Institut für Atmosphäre und Klima, 8092 Zürich, Switzerland.

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spectrometry [38–41], high performance liquid chromatography (HPLC) based methods [41–44] and ion chromatography [41,45–47] have been applied to unravel the complex chemical composition of ambient aerosol as well as particles generated in industrial processes. These approaches, although being highly selective and sensitive, have the drawback of being time-consuming and labour intensive.

Fast and in situ (i.e., no prior sample preparation) mass spectrometric techniques have been currently developed [48] enabling comprehensive and highly time-resolved studies of the chemical composition of aerosols as well as the investigation of single particles. Since the first on-line mass spectrometric analysis of single particles in 1973 [49], several concepts of aerosol mass spectrometry have been developed and realised [48]. Most of the developed on-line aerosol mass spectrometers can be divided into two classes according to the method of volatilisation of the PM's chemical constituents. These two classes are the laser based and the thermal heater based volatilisation methods, which are briefly described in the following.

1.1. Laser based volatilisation

Sinha [50] introduced the one-step laser desorption/ionisation (direct laser desorption and ionisation, LDI) process coupled to a quadrupole mass spectrometer for single particle characterisation. Since then several on-line single particle MS instruments were developed mostly based on time-of-flight mass spectrometry (TOFMS) [51–58] or ion trap mass spectrometry [59–61]. Single particle LDI mass spectra are dominated by electropositive species with low ionisation potentials such as metal cations (K^+, Na^+, Fe^+, etc.) and some cluster ions. In the negative LDI mass spectrum anions (e.g., chloride and sulphate) are detectable. However, analysis of organic species by single particle LDI-MS is difficult to achieve. In this context, PAH are only detectable from a particle matrix containing mainly elemental carbon (EC) or soot and if specific laser conditions are maintained [62]. Moreover, aliphatic compounds tend to be totally fragmented under conditions used in LDI experiments. Elemental carbon, however, is detectable with LDI-MS by means of carbon cluster ions while a rough sum value of organic carbonaceous matter can be estimated from organic fragment ions [63]. Recently Morrical et al. [64] and Lazar et al. [65] reported about the application of resonance enhanced multiphoton ionisation (REMPI [66–76]) for two-step on-line single particle aerosol mass spectrometry. The REMPI ionisation process is based on multiple photon absorption of target molecules in intense laser fields (laser pulses power density $>10^6$ W/cm^2), whereby the energy of the individual photons is lower than the ionisation potential. If the photon energy is in resonance with a molecular absorption band the efficiency of the multiple photon absorption (i.e., the ionisation) is considerably enhanced. Most aromatic compounds can be ionised very efficiently by laser pulses in the wavelength region 240–270 nm in an one colour two photon ionisation process (1 + 1 REMPI [70]). With a wavelength of 248 nm most PAH are ionised efficiently in a REMPI process [71]. This is particularly true when the molecules are warm, due to their broadened UV absorption bands. Morrical et al. used a CO_2-laser pulse (10.6 μm) for laser desorption and the fourth harmonic of a Nd:YAG laser (266 nm) for soft REMPI post-ionisation [64]. Mass analysis was carried out in a TOFMS system. In contrast Lazar et al. applied a XeCl excimer laser (308 nm) for desorption and a KrF excimer laser (248 nm) for REMPI post-ionisation followed by mass spectral analysis in an ion trap MS system. Instead of the UV-laser pulses used for REMPI VUV-laser pulses can also be used for post-ionisation of the desorbed species in a single photon ionisation (SPI) process [77,78]. The laser based SPI technique is more universal (i.e., can ionise more different compound classes) but also less sensitive in comparison to REMPI. It should be noted that laser desorption with laser post-ionisation has been very successfully applied for rapid off-line analysis of chemical species from PM loaded filters. If REMPI is used for the post-ionisation step, aromatic species such as PAH can be detected with very high sensitivity [79–85]. The application of laser based SPI for ionisation of laser desorbed aerosol samples allows the detection of aliphatic compounds such as acids or alkanes [86,87].

1.2. Thermal heat based volatilisation

The second group of aerosol mass spectrometric techniques uses a heated surface for volatilisation (i.e., thermal desorption, TD) of the impacted particles. The desorbed species are usually post-ionised by electron impact ionisation (EI) [88–93]. The generated ions are detected either by a quadrupole [89,90,94] or a time-of-flight mass spectrometer [93]. Due to the intense fragmentation caused by EI identification of distinct organic compounds on a molecular level is difficult. However, detection of sum values of organic compounds based on the observed fragment ions is claimed [95] and quantitative results are obtained [92]. The analysis of elemental carbon and mineral components, however, is not possible by thermal desorption.

In this technical note, we present an aerosol mass spectrometric set-up, which is based on the current LDI-TOFMS technology (e.g., LAMPAS [54] or ATOFMS [96]) but, in addition to single particle LDI, also allows single particle two-step laser desorption with REMPI laser post-ionisation (LD-REMPI with 10.6 μm laser pulse for desorption and 248 nm laser pulse for ionisation) as well as a quasi-on-line thermal heater desorption method with REMPI laser post-ionisation (TD-REMPI with a heatable impaction surface for desorption and 248 nm laser pulse for ionisation) for short-time enriched particle ensembles. In principle, the three modes LDI, LD-REMPI and TD-REMPI can be interchanged without any instrumental modification but activation of the respective lasers/heaters and by changing the respective trigger delays and the laser intensities. Hence, it is possible with the presented instrumental concept to analyse inorganic compounds by LDI using both polarities of the bipolar TOFMS on a single particle basis (LDI-ATOFMS) [58,97]. Furthermore, the relative contribution of elemental carbon and organic carbon (OC) can be estimated [63] from averaged single mass spectra. Using the laser desorption-REMPI post-ionisation (LD-REMPI-ATOFMS) is particularly efficient for the detection

Table 1
Summary of the different applied techniques

	On-line/off-line	Desorption	Ionisation	Sample type
LDI-ATOFMS (mode 1)	On-line	Excimer laser (KrF), $\lambda = 248$ nm, ~10^7 W/cm^2 one-step laser desorption/ionisation process (LDI)		Single particle
LD-REMPI-ATOFMS (mode 2)	On-line	CO_2-laser, $\lambda = 10.6$ μm, ~10^6 to 10^7 W/cm^2 laser desorption (LD)	Excimer laser (KrF), $\lambda = 248$ nm, ~1×10^7 W/cm^2 resonance enhanced multiphoton ionisation (REMPI)	Single particle
TD-REMPI-ATOFMS (mode 3)	Quasi-on-line	Heating rod $T = 300$ °C thermal desorption (TD)	Excimer laser (KrF), $\lambda = 248$ nm, ~1×10^7 W/cm^2 resonance enhancde multiphoton ionisation (REMPI)	Enriched particle ensemble

of PAH on a single particle basis while the thermal desorption-REMPI post-ionisation (TD-REMPI-ATOFMS) enables a short enrichment of particles on the surface of the (still cold) heater.

2. Experimental

Principles and technical features of the three operational modes of the instrument are summarised in Table 1. In addition, experimental set-ups and sketches of the occurring desorption and ionisation processes are presented: LDI-ATOFMS (Fig. 1A and B), LD-REMPI-ATOFMS (Fig. 1 A and C) and TD-REMPI-ATOFMS (Fig. 1A and D). Particles enter the instrument through a dual-chamber three-nozzle system (Scientific Instruments GBR, Spengler & Hinz, Linden, Germany). Diameters of the nozzles are 400, 300 and 500 μm. The expanding carrier gas is pumped out differentially. The first stage is pumped by a rotary pump (Pfeiffer Vacuum GmbH, Asslar, Germany; model, DUO 20; pumping speed, 21 m^3/h) to a working pressure of 11 mbar. Working pressure of the second stage is in the range of 5×10^{-2} mbar by employing a turbomolecular pump (Pfeiffer Vacuum GmbH; model, TMH 261-010). The third stage (ion source) is pumped by a turbomolecular pump (Pfeiffer Vacuum GmbH; model, TMU 521 to a final pressure of 2×10^{-6} mbar). Particles along the centre line of the inlet pass two continuous wave sizing laser beams (Laser Star GmbH, Reno, USA; model, GCL050-L, $\lambda = 532$ nm), whereby the distance between the sizing laser beams is 12 mm and the distance from the lower sizing laser beam to the centre of the

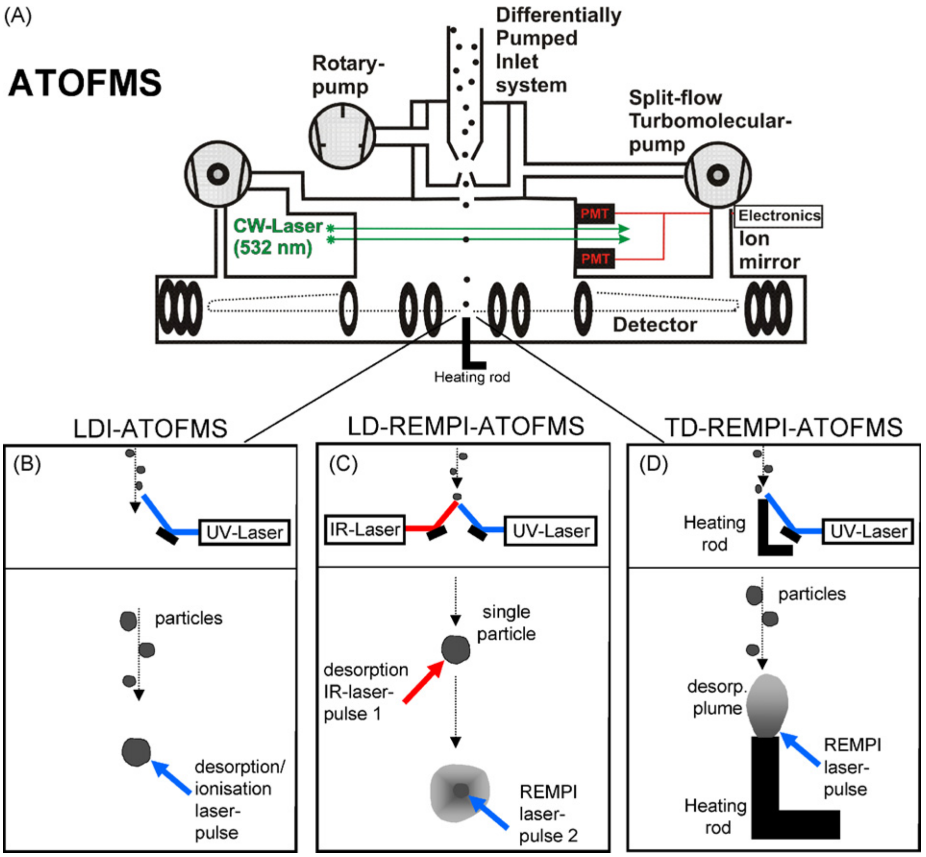

Fig. 1. Sketch of the ATOFMS instrument (A). Drawing of the LDI-ATOFMS (B), LD-REMPI-ATOFMS (C) and TD-REMPI-ATOFMS (D) technique.

ionisation region of the bipolar time-of-flight mass spectrometer (Kaesdorf Instruments, Munich, Germany) is 24 mm. Scattered light is detected by photomultipliers (PMT, model 931B, Hamamatsu). A custom-made electronic device (Jungbauer, VRPE Team GmbH, Germany) is used for measuring the time period between the scattering events from the two sizing laser beams for determination of the aerodynamic diameter of the tracked particles and, therefore, the size-dependent triggering of the LDI or LD laser pulse. Polystyrene latex particles were used for the size calibration similar as described in [98]. For LDI-ATOFMS a KrF excimer laser (Lambda-Physik GmbH, Goettingen, Germany; model, OPTEX) generating a wavelength of 248 nm was used for the single step laser desorption/ionisation process. The laser power was set to about 1×10^7 W/cm^2 [62]. In the LD-REMPI-ATOFMS mode a CO_2-laser was applied for the laser desorption process (CO_2-laser, model, MTL-3, Edinburgh Instruments Ltd., Scotland), which generates 10.6 μm pulses with a peak energy of ca. 50 mJ, a peak width of 50 ns and a power density of 10^6 to 10^7 W/cm^2 in the focus. The power density of the KrF excimer laser for REMPI was $\sim 10^7$ W/cm^2. The delay between firing of the CO_2-laser and the following excimer ionisation laser was in the range of 0.5–4 μs. The desorption and ionisation lasers were spatially overlapping in the centre of the TOFMS ion source. However, in order to compensate for the motion of particles and desorption plumes during the delay time, the central focus point of the desorption laser was shifted 0.5 mm upstream the particle beam with respect to the focus of the ionisation laser.

For the TD-REMPI-ATOFMS (Fig. 1D) mode a heating element (Watlow GmbH, Kronau, Germany; model, cartridge heater; Ø 6 mm) was implemented for thermal desorption of particles precipitated on the heater-surface. The cylindrical heating rod made of stainless steel was placed directly in between the repeller and the extraction electrode, about 8 mm underneath the ionisation centre of the TOFMS. The particle beam hits the front surface of the heating rod. One possible disadvantage of the used simple heater design is the possibility of bouncing-off effects of particles as observed in thermal desorption—electron impact MS [89,99]. Further investigations regarding the heater design are required in the future.

After a collection period of about 10 min with the heating off the impacted particles were evaporated by quickly heating up to a temperature of ca. 350 °C. The desorbed molecules were ionised by 248 nm laser pulses from the excimer laser (pulse width 8 ns, power density approximately 1×10^7 W/cm^2).

The mass spectra of the positive ion flight tube (LDI- and LD-REMPI-ATOFMS) and the negative ion flight tube (LDI-ATOFMS) of the bipolar TOFMS were recorded via two transient recorder PC cards (Aquiris, Switzerland, 250 MHz, 1 GS/s, 128 kb). Subsequent data processing was done by a LabView (National Instruments, USA) based on custom-written software. Data acquisition for the TD-REMPI-ATOFMS experiments (car exhaust) was carried out by using a digital storage oscilloscope (LeCroy Corporation, Chestnut Ridge, USA; model, Waverunner 6050A). Data analysis was performed with custom written LabView Software Routines and Origin (6.0). A small scale powder disperser (model 3433 SSPD; TSI Inc., St. Paul, USA), which allows the dispersion of powders or agglomerated material in small quantities, was applied for testing the instrument in the laboratory. In so doing, greyish spruce wood ash from a lambda probe-controlled wood fired 20 kW residential heating system was investigated in the LDI-ATOFMS and the LD-REMPI-ATOFMS mode. In addition to that, exhaust fumes of a gasoline driven passenger car (Ford Escort; model 1997) with a controlled catalytic converter were analysed in a first on-line monitoring experiment with the TD-REMPI-ATOFMS mode of the instrument.

3. Results and discussion

Mass spectra obtained with the triple-mode aerosol mass spectrometer are presented in Fig. 2A–D. Using the LDI-method, positive and negative single particle mass spectra are recorded. In Fig. 2A and B the positive and the negative LDI-ATOF mass spectra of a single 1.1 μm spruce wood ash particle are shown. The positive spectrum exhibits peaks at 23 *m*/*z*, 39 *m*/*z*, 41 *m*/*z* and 56 *m*/*z*, which can be assigned to the elemental ions sodium, potassium and iron. In the negative mass spectrum the hydroxyl anion and a pronounced carbon cluster series from C_2 to C_7 is observable as well as the complex conjugated anions of the hydrocyanic, cyanic, nitrous and sulphuric acid. The obtained LDI mass spectra are very similar to the LDI single particle mass spectra of wood ash from reference [100]. Although the 248 nm laser power density of $\sim 10^7$ W/cm^2 was in the optimal range for PAH detection from (soot) particles [62], only in less than 1% of the LDI spectra very weak signals in the PAH mass region are detectable, which, however, often do not correspond to typical PAH masses. The incapability of LDI-ATOFMS to detect PAH signatures can be readily explained by the known LDI matrix effects: PAH are not detectable by LDI when the matrix mainly consists of mineral compounds and salts and exhibits low amounts of EC [62,101,102] Consistently, the conventional chemical analysis of the wood ash particle sample (bulk; Table 2) depicted that the ash is burned out very well having an EC content of only 1.5%. Thus, the LDI-ATOFMS results confirm the “matrix” problem of single step laser desorption/ionisation for detection of organic aerosol constituents. In order to detect the PAH species the second operational mode of the aerosol mass spectrometer is applied using an IR laser pulse for desorption of the particle in the first step. The intense IR laser pulse efficiently desorbs molecular species and, as a consequence, separates them from the solid particle matrix. It should be noted that laser desorption is more shock wave driven than being a thermal process. Thus, the temperature of the desorbed molecules is comparable low [103]. The separation of the molecules from the solid particle matrix allows the application of gas phase ionisation mechanisms. Due to its sensitivity and selectivity the method of choice for analysing aromatic compounds in the desorption plume is REMPI. Fig. 2C shows a spectrum obtained with the instrument using the LD-REMPI-ATOFMS approach. In contrast to LDI, PAH such as phenanthrene $C_{14}H_{10}$ ($m/z = 178$), pyrene $C_{16}H_{10}$ ($m/z = 202$), chrysene, triphenylene and benzo[*a*]anthracene $C_{18}H_{12}$ ($m/z = 228$), benzopyrenes and benzofluoranthenes

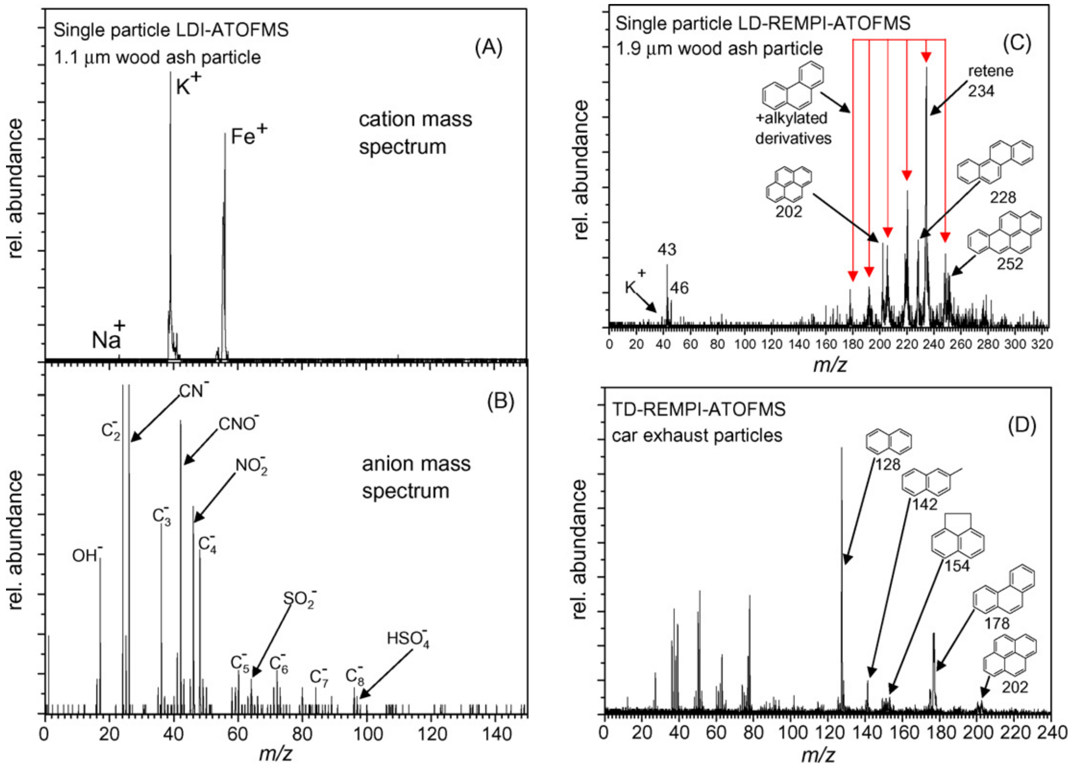

Fig. 2. (A) LDI-ATOFMS cation mass spectrum of a 1.1 μm single wood ash particle. (B) LDI-ATOFMS anion mass spectrum of the same 1.1 μm wood ash particle as in (A). (C) LD-REMPI-ATOFMS mass spectrum of a single wood ash particle. The separation of the desorption step (CO_2-laser, λ = 10.6 μm) and the ionisation step (excimer laser, λ = 248 nm (REMPI)) allows the detection of PAH. (D) On-line measured TD-REMPI-ATOFMS spectrum of gasoline car exhaust particles. Several PAH such as naphthalene (128 *m/z*) and homologues, acenaphthalene (152 *m/z*), phenanthrene (178 *m/z*) and pyrene (202 *m/z*) can be observed.

$C_{20}H_{12}$ (m/z = 252) are clearly visible. In addition, homologue series of alkylated phenanthrenes can also be observed (marked in Fig. 2C). For better evaluation of the results the spruce wood ash (bulk sample) was analysed for PAH by conventional GC–MS. Furthermore, some inorganic ions and the sum values of the carbonaceous fractions were determined. The results of the conventional measurements on the bulk ash sample are summarised in Table 2. The sum of the analysed PAH was about 280 mg/kg. The alkylated phenanthrene compound retene (1-methyl-7-isopropylphenanthrene, 234 *m/z*) was identified as main PAH component (41 mg/kg) in the wood ash. The total level of PAH in the investigated wood ash sample is not very high. For example, Schauer et al. obtained 20 times higher retene concentrations (about 900 mg/kg emitted fine particulate matter) in emission of an open pine wood fire [104]. The 234 *m/z* mass peak in the single particle LD-REMPI-ATOFMS mass spectra can be surely assigned to retene, as it is by far the most abundant C4-phenanthrene isomer (>90%) according to

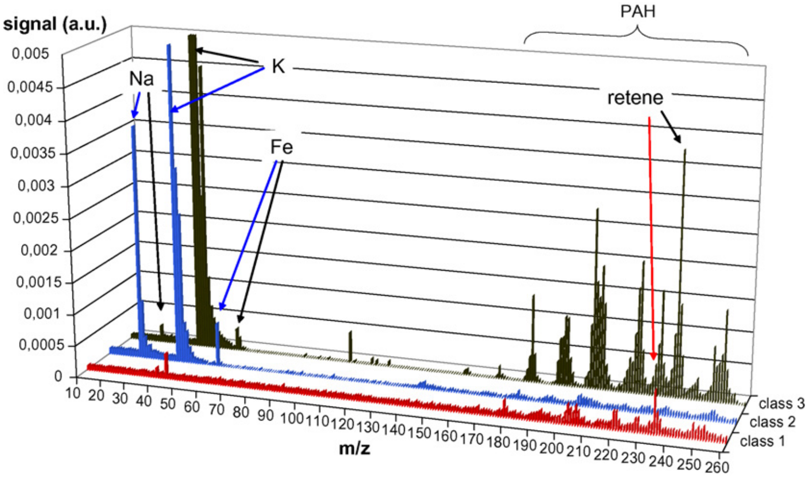

Fig. 3. Averaged mass spectra of wood soot analysed by LD-REMPI sorted by types: (Class 1) spectra showing mass 234 but not mass 39 with S/N ≥3 (“pure” PAH spectra); (Class 2) spectra showing mass 39 but not mass 234 with S/N ≥3 (“pure” inorganic spectra); (Class 3) spectra showing both mass 39 and mass 234 with S/N ≥3 (mixed spectra). S/N level was calculated by standard deviation of mass trace m/z = 10.

Table 2
Conventional analysis of wood ash carried out by DTD-GC-TOFMS (PAH, retene), ion chromatography (inorganic anions except carbonate), ICP-OES (inorganic cations) and carbon analysis (oxidative/thermal released carbon dioxide after suitable preparation)

Compound/parameter	*m*/*z*	Concentration (bulk)	
PAH			
Phenanthrene	178		29 μg/g
Fluoranthene	202	61 μg/g	
Pyrene	202	79 μg/g	$\sum_{202}$: 140 μg/g
Benzo[*a*]anthracene	228	26 μg/g	
Chrysene	228	50 μg/g	$\sum_{228}$: 76 μg/g
Benzofluroanthenes	252	22 μg/g	
Benzo[*a*]pyrene	252	6 μg/g	
Benzo[*e*]pyrene	252	10 μg/g	
Perylene	252	1 μg/g	$\sum_{252}$: 39 μg/g
Benzo[*ghi*]perylene	276		2 μg/g
Organic wood burning indicator			
Retene	234		41 μg/g

Inorganic ions	*m*/*z*	LDI-ATOFMS signal	Concentration (bulk) (%)
K	39/41	√	5
Ca	40	√	24
Mg	24	–	3
Mn	55	–	3
Fe	56	√	1
SO_4	96	√ (SO_2)	4.5
NO_3	53	√ (NO_2)	0.6
Cl	35/37	–	1.8

Sum values of carbon compounds	Concentration (bulk) (%)
EC	1.5
OC	8.2
TC (EC, OC and carbonates)	16.6

the GC–MS measurements (retention time and mass spectrum is matching with retene standard). Retene is a known marker for coniferous wood [104]. As all LD-REMPI-ATOFMS spectra with PAH signals show a very prominent retene signal, 234 *m*/*z* peak may be a good source indicator for coniferous wood combustion related particles in single particle LD-REMPI-ATOFMS investigations. LD-REMPI-ATOFMS spectra of other biomass burning particles, e.g., from cigarette smoke, do not show an intense 234 *m*/*z* peak in the PAH signature [64]. By comparison to the single ion signal it can be estimated that the 234 *m*/*z* peak in Fig. 2C is originated by about 500 retene ions reaching the surface of the multichannel plate (MCP) detector. With the LD-REMPI-ATOFMS technique more than 30% of the obtained mass spectra show PAH signals (measured at the mass of retene, 234 *m*/*z* with $S/N \geq 3$) for a delay time of 1.5 μs between laser desorption and REMPI laser pulses. It is interesting to note that there is a dependence of the observable typical ion species from the delay time. If the delay time is set to 0.5–1.5 μs, the optimum time range for the intensity of the single-particle PAH signal, also intense 23/39/40/41 *m*/*z* and 56 *m*/*z* peaks from LDI-type ionisation of Na, K, Ca and Fe appear in many spectra. The reason is that due to the overlap of the desorption and ionisation pulse the particle is also hit by the KrF excimer laser pulse after the desorption pulse. Therefore, we have overlying LDI signals form the particle core and REMPI signals for the post-ionised desorption plume. Note that at extended delay times it is possible to separate the LDI and REMPI processes to solely obtain REMPI spectra. However, as in this case only a minor part of the desorption plume can be addressed by the REMPI ionisation laser the overall intensity decreases considerably. At delay times around 1 μs the particles are definitely hit by both lasers. The obtained single particle spectra from the spruce wood ash sample can be grouped into three classes (Fig. 3). The first class contains spectra which only depict organic PAH signatures (∼10%), the second class contain only inorganic signatures (∼30%) and the third class shows mixed signatures of PAH and inorganic compounds (∼60%) such as K, Na and Fe. If compared with the LDI results, where no usable PAH signals could be retrieved, it is obvious that the separation of laser volatilisation and laser ionisation is by far more efficient for detection of PAH in single particle mass spectrometry. In an averaged LD-REMPI-ATOF mass spectrum of a large number of particles (all classes) the retene signal typically is about 10 times higher than the $S/N \geq 3$ level. If we assume for a rough sensitivity estimation that the PAH containing particles (Class 1 and Class 3) are evenly distributed over the size (as we only cover particles from 0.5 to 10 μm) – which is probably not perfectly true – we could calculate a retene detection limit in the region of 4 mg/kg. For establishing a more precise LD-REMPI-ATOFMS detection limit on a single particle basis in the future, however, it will be necessary to generate standard particles with homogenous analyte concentrations.

The LD-REMPI-ATOFMS results show the potential of organic single particle mass spectrometry. Future studies will also concentrate on the investigation of different particle sources and detection of single particles from ambient air at the GSF super site aerosol measurement station in Augsburg, Bavaria. Particularly interesting is the search for further source tracers, such as retene for coniferous wood combustion related particles in the here presented work. A system consisting of two lasers, which need to be aligned precisely regarding delay time, beam profile and spatially position is, of course, less field-deployable than the single laser systems [58,105] or thermal desorption EI post-ionisation aerosol mass spectrometric based techniques [99]. Another problem in single particle mass spectral analysis is the coverage of small particles, which cannot be efficiently detected by the sizing system anymore. Furthermore, the absolute amount of available material of trace compounds is quickly decreasing with decreasing particle diameter. A hypothetical, compact and spherical particle of density 1 g/cm^3 with a diameter of 1 μm has a mass of 500 femtogram (fg). Assuming a sum concentration of 40 μg/g for a PAH species of 252 *m*/*z* (or the 234 *m*/*z* retene molecule) about 50,000 molecules are present in the particle. With a reasonable estimated REMPI efficiency of 5%, a TOF transmission rate of 10% and a MCP detection efficiency of 50% only ca. 125 ions would be detected in the case of quantitative desorption (which is unlikely). As the hypothetical amount of PAH or retene molecules decreases to 6000 for a particle with a diameter of 0.5 μm and to 400 for a particle with 200 nm diameter the detection probability of trace compounds quickly decreases with smaller particle diameter. Thus, for a 200 nm particle only 1 ion will be detected. If REMPI is replaced by the more universal but less sensitive laser based SPI this problem is even more prominent. Therefore two-step single particle mass spectrometry of aliphatic organic compounds with a SPI post-ionisation step will be possibly restricted to larger particles and major compounds or model particles made from one or a few pure organic compounds [78] or to detection of laser desorbed particle ensembles [86,87].

As a result of the above mentioned problems to obtain organic information with single particle mass spectrometry the thermal desorption method was implemented in the instrument. The laser desorption step is replaced by a thermal desorption unit based on a heatable rod, which was mounted between the two electrodes of the ATOFMS. Sampling on the rod even enables to characterise particles, which feature a size below the lower limit of the sizing system (0.4 μm) and, therefore, are not accessible by the single particle modes at all. Before heating particles were collected on the cold rod for about 10 min. The aim of this approach is to enhance the detectability of low particle-bound PAH concentrations by a short enrichment step. The enrichment concept is rather similar to the one described by Tobias et al. [89,90], where particles were desorbed in a temperature programmed thermal desorption procedure and the desorbed species detected by EI-quadrupole mass spectrometry. After thermal desorption, the volatilised aromatic species were REMPI post-ionised followed by time-of-flight mass spectrometric detection (TD-REMPI-ATOFMS). Fig. 2D shows a quasi-on-line TD-REMPI-ATOFMS mass spectrum of particles from car exhaust (average over 10 laser shots). The PAH naphthalene (128 *m*/*z*) and homologues, acenaphthalene (152 *m*/*z*), phenanthrene (178 *m*/*z*) and pyrene (202 *m*/*z*) can be observed. It should be noted that the heater's position and surface as well as the REMPI detection scheme is not yet optimised, thus the TD-REMPI-ATOFMS result is still of preliminary character. However, the principal benefit of TD-REMPI-ATOFMS, namely the possibility of enriching particles on the heatable rod by extending the sampling period on the cold heater, is demonstrated. Because of the more complete evaporation of the non-refractive constituents of the particulate matter improved quantification properties should be possible similar as in the TD-EI-MS approach of the commercial AMS-system [93,106]. Technologies for size selective deposition of particles as well as methods for enrichment of ultra fine particles on the heater (i.e., aerodynamic lens inlet and chopper systems) are well established [93,94,99] and can be adapted to the system. Although the results obtained with the thermal desorption are still of preliminary character it can be stated that one important benefit of the here presented instrumental concept is the possibility to perform LDI-ATOFMS, LD-REMPI-TOFMS as well as thermal desorption based methods in one single instrument. In the future the maximal repetition rate of the excimer laser (200 Hz) will be used for increasing the duty cycle of TD-REMPI measurement using a transient recorder card with direct averaging for data acquisition. Furthermore, single photon ionisation – either with a laser based VUV source [107] or with a novel intense and brilliant electron pumped rare gas excimer VUV lamp [108,109] – will be implemented to increase the accessible organic compound classes.

4. Conclusion

The here presented work demonstrates the potential of soft photo ionisation for detection of organic trace compounds in aerosol mass spectrometry. The built aerosol mass spectrometer combines three different detection modes in one device. LDI-ATOFMS is suitable for analysis of inorganic compounds (anions and cations) and – with restrictions – for determination of the sum values of elemental and organic carbon content. LD- and TD-REMPI-ATOFMS are especially sensitive for the detection of aromatic trace compounds due to the separation of compound volatilisation and ionisation as well as due to the soft ionisation capabilities provided by REMPI. Single particle analysis of PAH is possible with the LD-REMPI-ATOFMS technique, whereas TD-REMPI-ATOFMS covers enriched particle ensembles deposited on the cold rod during a short enrichment time. Further development of the instrumental concept is leading towards a universal aerosol mass spectrometer, which comprehends thermal and laser based single particle volatilisation as well as REMPI, SPI and EI ionisation methods for comprehensive on-line aerosol characterisation.

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