A solid-state IR laser for two-step desorption/ionization processes in single-particle mass spectrometry

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Abstract. Recent advancements in single-particle mass spectrometry (SPMS) have enabled the detection of aromatic hydrocarbons at the individual particle level in conjunction with inorganic/refractory particle components. However, the laser desorption (LD) of organic material from particles prior to their ionization in a two-step process necessitates pulsed infrared lasers with adequate pulse energy that can be irregularly triggered on detected particles. Pulsed CO_2 lasers with a 10.6 μm wavelength have been traditionally utilized, yet these lasers are bulky, costly, and require regular maintenance, including gas exchange or a continuous laser gas supply. In this study, we present the application of a prototype solid-state laser based on an erbium-doped yttrium aluminum garnet (Er:YAG) crystal, emitting long pulses of 200 μs at 3 μm wavelength as a compact, cost-effective, and user-friendly alternative for LD. We directly compared the new laser with a commonly used CO_2 laser and found similar performance in LD for both laboratory particles and ambient air experiments. With the exception of slightly increased fragmentation observed with the CO_2 laser due to its beam profile, no qualitative differences were noted in the resulting mass spectra. Additionally, we compared the novel two-step ionization scheme for the combined detection of aromatic molecules and inorganics with conventional single-step laser desorption/ionization (LDI) for the detection of polycyclic aromatic hydrocarbons (PAH) in laboratory and field experiments. The combined methods demonstrated superior performance in the detection of PAHs, for both the CO_2 and the new Er:YAG laser. In addition to its higher sensitivity and lower fragmentation for PAHs when compared to single-step LDI, it is less dependent on the particle matrix, sharing the benefits of traditional two-step methods but extending its capability to combine PAH measurements with the LDI-based detection of inorganic particle compounds.

1 Introduction

30   Single-particle mass spectrometry (SPMS) has significantly expanded our understanding of aerosols and atmospheric processes due to two inherent characteristics of the technique. (I) By desorbing and ionizing individual particles using laser pulses, SPMS reveals the mixing state of the particle ensemble, i.e., the distribution of chemicals within individual particles. This allows the detection of subpopulations of particles, their sources, and the investigation of atmospheric processes in complex aerosols. (II) Unlike prevalent bulk methods based on thermal desorption, such as the Aerodyne Aerosol Mass

35   Spectrometer (AMS) or proton transfer reaction-based methods for aerosols (Reinecke et al., 2024a, 2024b), SPMS also captures refractory particle compounds like metals and mineral dust components (Pratt and Prather, 2012; Passig and Zimmermann, 2021; Laskin et al., 2018; Marsden et al., 2019; Zawadowicz et al., 2017; Passig et al., 2020).

In most SPMS instruments, particles are hit by intense, focused UV laser pulses to create a sufficient ion signal for less abundant particle components via laser desorption/ionization (LDI). With few exceptions, organic molecules are fragmented

40   in this process, making their speciation difficult. In contrast to the use of single UV laser pulses for LDI, so-called two-step approaches first use an IR laser pulse to vaporize the organic matter from the particle, and a second UV laser pulse to hit the resulting plume and ionize the molecules in the gas phase. The separation of laser desorption (LD) and ionization allows the independent optimization of both processes. This has several advantages: while LD alone is still a complex process resulting in the vaporization of molecules at high temperatures, the laser intensities and photon energies can be much lower compared

45   to LDI, reducing fragmentation (Schmidt et al., 2023). Because ionization occurs in the gas phase, matrix effects are reduced which is beneficial for quantifying approaches (Woods et al., 2001). In addition, gas-phase ionization allows for very soft ionization techniques such as single-photon ionization (SPI) (Nash et al., 2005; Hanna et al., 2009) or resonance-enhanced multiphoton ionization (REMPI) (Gehm et al., 2018). The latter is particularly useful for SPMS because the involved resonances make it very sensitive – a key characteristic when dealing with such small sample volumes as plumes surrounding

50   tiny particles – and it selectively ionizes aromatic molecules with very high efficiency. This is of great benefit for aerosol studies because it detects carcinogenic polycyclic aromatic hydrocarbons (PAHs), ubiquitous air pollutants from combustion processes, and major contributors to the health effects of aerosols (Agudelo-Castañeda et al., 2017; Holme et al., 2019). The two-step LD-REMPI method, introduced in SPMS by Morrical et al. (1998), has been used by a few groups to study PAHs at the single-particle level, e.g., to identify sources of PAHs in ambient air pollution (Bente et al., 2009) or to analyze particles

55   for studying aging effects (Li et al., 2019). One significant disadvantage of these two-step approaches is the missing particle composition from LDI, i.e., the metals, salts, etc.

This constraint has been successfully addressed, first by implementing a series of three laser pulses for LD, REMPI, and LDI in a rather complex setup that enables the measurement of only positive ions (Passig et al., 2017). Meanwhile, a novel technique has been devised to leverage the spatial segregation of the gas plume from the particle residue, enabling the integration of

60   REMPI and LDI into a single laser pulse with a customized radial profile and yielding bipolar LDI spectra in addition to the

PAH signatures (Schade et al., 2019; Zimmermann et al., 2019). The latter method has been successfully applied in ambient air studies and laboratory experiments, showing its potential for source apportionment, new monitoring concepts, and investigations of atmospheric processes (Passig et al., 2022; Anders et al., 2023; Anders et al., 2024). There are also hybrid approaches where LD is applied prior to LDI at 193 nm to reduce organic fragmentation and matrix effects, and has been shown to result in highly reproducible mass spectra with significantly less particle-to-particle variation, while providing LDI mass spectra comparable to many other instruments (Zelenyuk et al., 2015; Zelenyuk et al., 2009).

To date, all two-step methods in SPMS are based on transversely excited atmospheric pressure (TEA) CO_2 lasers, because these systems provide relatively strong and short mid-IR pulses (multi-mJ, $\approx$ 50–500 ns duration, 10.6 µm wavelength). These lasers are relatively large and expensive, and they have one major disadvantage: they require regular gas changes or even operation with a constant gas flow. The required gas supply limits the use of CO_2-TEA lasers in field studies, especially in situations where aerosol measurements are urgently needed: in arctic regions, on the open sea, in remote areas with limited infrastructure, and for remote controlled long-term operation. For the ionization step in two-step approaches, frequency-quadrupled Nd:YAG lasers at 266 nm offer a low-cost, robust, and maintenance-free alternative to excimer gas lasers. However, a similar solution is still lacking for the LD step.

Here we report on experiments to replace the CO_2 lasers with a prototype Er:YAG solid-state laser at 3 µm wavelength. We evaluate its performance in direct comparison experiments and discuss its potential and limitations in future applications. Besides, we performed comparative experiments and demonstrated superior detection of PAHs using two-step approaches compared to conventional LDI, regardless of the type of laser used for LD.

2 Experimental Section

2.1 Model Particles and Sampling

Laboratory experiments were performed for three different types of PAH-containing particles. (I) Diesel exhaust particles were collected from an old van (VW Transporter type 3, 1.7 D, no exhaust aftertreatment), directly scratched from the inner surface of the exhaust pipe. These particles have a uniform chemical distribution of PAHs from regular exposure to the hot exhaust gas (Passig et al., 2017; Schade et al., 2019). (II) Wood ash particles were collected from an ash sink in the chimney of a 20 kW wood combustion furnace (Bente et al., 2008). Using a small-scale powder disperser (model 3433 SSPD, TSI Inc., St. Paul, MN), diesel soot and wood ash particles were redispersed into a synthetic air stream of 2.5 L min⁻¹, from which 100 mL min⁻¹ was introduced into the SPMS system. (III) Tar ball particles were used as a proxy for organic aerosols (Li et al., 2019). The term tar ball refers to near-spherical, homogeneous particles resulting from the combustion of biomass and biofuels and consisting of amorphous carbonaceous species (Pósfai et al., 2004; Hand et al., 2005; Alexander et al., 2008). To produce the tar ball particles, beechwood tar from a hunting supply store was dissolved in methanol, sprayed with an aerosol generator

(ATM 221, Topas GmbH, Germany), and dried using a custom diffusion dryer with a silica gel-filled cartridge. Size distributions of the particles are shown in the supplementary information, Fig. S1.

The ambient air experiments were performed at the ILMARI laboratory of the University of Eastern Finland in the timeframe from March 1, 2024 to March 3, 2024. To record a sufficient number of single-particle spectra from the relatively clean air

95 ($PM_{10} < 4.0$ µg m^{-3} in average), ambient air particles were sampled using an aerosol concentrator (AC-250 v1.0, ParteQ GmbH, Germany). The instrument is based on an advanced design of the discontinued Model 4240 (MSP Corp., now part of TSI Inc., U.S.A.) and concentrates particles in the size range of approximately 0.5–10 µm from a 250 L min^{-1} inlet flow into a 1 L min^{-1} sample stream (Romay et al., 2002). After passing through a dryer (model MD-700-12S-1, Perma Pure LLC, USA), the aerosols underwent additional concentration to 0.1 L/min through a further virtual impactor at the SPMS aerodynamic lens

100 (Zhuo et al., 2021). The instrument's overall detection efficiencies for the particles used in this study were not determined (Shen et al., 2019).

2.2 SPMS Instrumentation

The basic principle of SPMS systems relies on the optical detection and sizing of aerodynamically accelerated particles before LDI and ion detection in a bipolar time-of-flight mass spectrometry setup (Passig and Zimmermann, 2021; Pratt and Prather,

105 2012).

The instrument utilized here has been previously described (Schade et al., 2019) and roughly corresponds to the setup commercialized as PhotonLIZA (Photonion GmbH, Germany). A KrF excimer laser (248 nm, PhotonEx, Photonion GmbH, Germany) is used for ionization after laser desorption. The ion signals, from both cations and anions, were recorded by a 14-bit digitizer card with one channel per polarity (ADQ14, Teledyne SP Devices AB, Sweden) and were analyzed using custom

110 Matlab software, including preprocessing and peak area integration. Classification of the PAH mass spectra from ambient air particles was performed using the adaptive resonance theory neural network ART-2a (Song et al., 1999) from the open-source toolkit FATES (Sultana et al., 2017) using a vigilance factor of 0.75, a learning rate of 0.05, and 20 iterations.

2.3 Optical setup and triggering

In the two-step mode, the particles entering the ion source are exposed to an IR laser pulse for LD, and the gaseous plume is

115 then irradiated with an unfocused UV pulse of medium intensity for soft REMPI of aromatic species. This layout is illustrated in Fig. 1a and was used to study the LD with the Er:YAG laser in comparison to the CO_2 laser for the laboratory particles and the first of two ambient air experiments. To allow a direct comparison of the prototype Er:YAG laser (Er:YAG 1000 FQ, InnoLas Laser GmbH, Germany) with the standard CO_2 laser (Model EX5, GAM Laser Inc., USA), the setup was modified as follows: the two IR lasers were alternately fired from opposite sides of the ion source at the incoming particles; see Fig. 1a and

120 the time cycle included therein. A noise signal characteristic for each laser was imprinted in the mass spectra to ensure the

assignment of each laser to the resulting single-particle spectrum. In this configuration, each particle was detected twice, and size data was recorded along with mass spectra as in normal operation. However, the individual particle size data could not be directly linked to individual spectra, meaning only average size distributions could be obtained. This "alternate firing" setup allowed for simultaneous measurement of the same aerosol and even ambient air, ensuring that the only variable was the LD laser.

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The CO_2 laser and the Er:YAG laser vary not only in their wavelengths but also by several orders of magnitude in their pulse lengths; see Table 1 for detailed optical parameters. This is due to the lack of Q-switching for the Er:YAG laser. Within the 200 µs pulse duration, the particles travel a distance of approximately 1-2 cm. Therefore, the laser is not focused but sent, with its full spot size of 5 mm, into the region above the ion source. The reduced spatial and temporal accuracy requirements

130 facilitate alignment in comparison to the CO_2 laser. The lower power density of the Er:YAG pulse is compensated by the longer exposure time for each individual particle and by the 10 times higher pulse energy. It should be noted, that the pulse-to-pulse energy variation of the Er:YAG laser was large (up to ± 50 % calculated on the average pulse energy, a histogram of pulse energies can be found in Fig. S2). This is a result of unstable thermal lensing in the resonator, as this prototype laser was not optimized for random triggering from the incoming particle events. To reduce this, a regular signal of 5 Hz was mixed into

135 the trigger input. The total reduction in hit rate resulting from the combined loss in duty cycle and pulse-to-pulse variations is estimated to be ≈ 30–50 %, compared to a hypothetical stable Er:YAG laser to be developed for irregular triggering in SPMS. However, this is only a rough estimation because the pulse energy required to generate a sufficient plume is highly dependent on the particle properties and composition.

140 **2.4 The Er:YAG laser for laser desorption**

The Er:YAG system is a flashlamp-pumped solid-state laser that uses an erbium-doped yttrium aluminum garnet ($Er:Y_3Al_5O_{12}$) crystal as its active medium, emitting at a fundamental wavelength of 2940 nm. The system comprises a water-cooled laser head (dimensions: 35.8 cm × 11 cm × 6 cm; weight: 3.9 kg) and a power supply unit (dimensions: 46.8 cm × 21.5 cm × 49.5 cm; weight: 21 kg). The maximum pulse repetition rate is approximately 50 Hz; however, at higher repetition rates exceeding

145 20 Hz, the pulse energy decreases, and its fluctuations increase. The beam profile is super-Gaussian, trending toward a flat-top intensity distribution.

This laser was specifically designed for the application, delivering long pulses (200 µs) with high pulse energy (> 300 mJ). Its high pulse energy eliminates the need for focusing to generate a gas plume from particles, significantly simplifying alignment relative to the particle beam compared to focused lasers. Additionally, the extended pulse duration reduces the laser intensity

150 experienced by the particles, minimizing excessive heating and fragmentation. Further details on the system's optical properties are presented in Table 1.

2.5 Implementation in the combined ionization scheme for PAHs and inorganics

At the end of this paper, we present an additional experiment on ambient aerosols to demonstrate the suitability of the Er:YAG laser for the newly developed ionization in SPMS that combines REMPI and LDI in a single laser pulse (Schade et al., 2019), and we compare this method directly with a conventional LDI-based setup. In the combined setup (Fig. 1b), the unfocused beam inducing REMPI with moderate laser intensity is reflected by 180°, is focused, and sent back into the ion source. There, it hits the refractory particle residue, inducing LDI at virtually the same time as the PAHs are ionized in the gas plume via REMPI. The comparison with conventional LDI was realized as follows (Fig. 1, bottom): One particle event triggered the CO_2 laser for LD, followed by the excimer laser for combined ionization. The second particle triggered the same scheme with the Er:YAG laser instead of the CO_2 laser for comparison. The third particle triggered none of the LD lasers but only the excimer laser. As no prior LD occurred and no gas plume was produced, only the back-reflected beam induced LDI, similar to conventional LDI ionization, with an excimer laser focused by a lens. All triggering schemes were realized using a Complex Programmable Logic Device (CPLD) microcontroller and custom software.
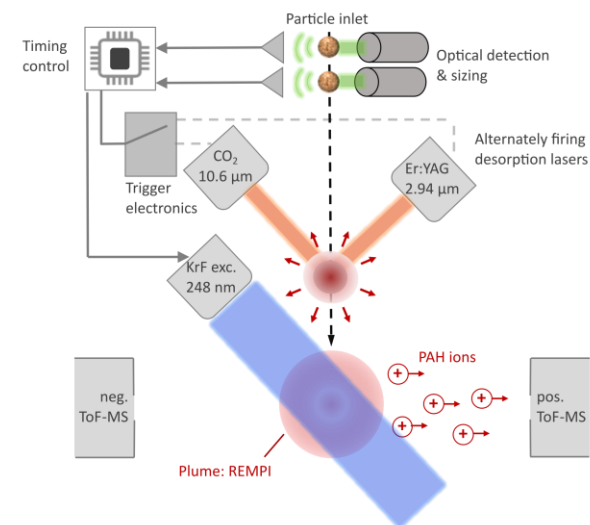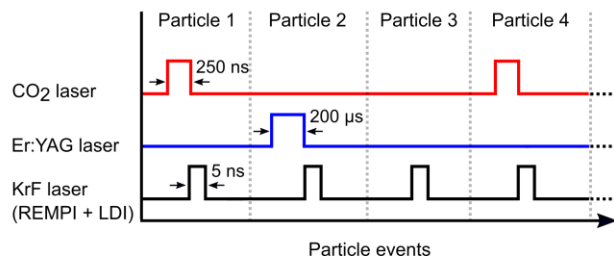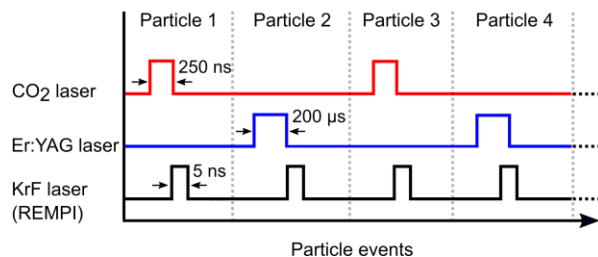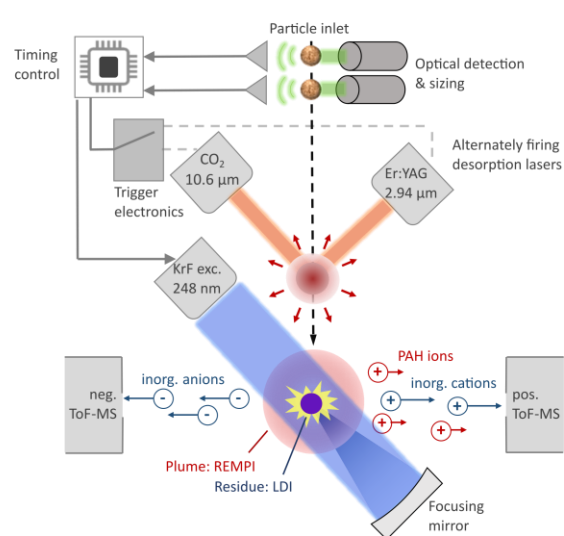
Figure 1 (a) Schematic representation of the single-particle, two-step ionization setup in alternating mode for direct comparison of the two desorption lasers. The particles are optically detected, initiating the SPMS time cycle. In the ion source, the two desorption lasers, i.e., the "standard" CO_2 laser and the experimental Er:YAG laser, are alternately fired at the respective particles, generating a small gas plume for each particle. Few µs later, the unfocused UV laser pulse ionizes the PAHs in the expanding plume via REMPI. Scheme **(b)** shows the combined method to ionize PAHs by REMPI in the unfocused beam and inorganics by LDI in the back-reflected and focused beam, both from the same laser. In addition to the comparison of the CO_2 laser and the Er:YAG laser for LD in this method, every third particle was not exposed to IR LD laser. In this case, only the intense back-reflected UV pulse interacted with the particle, inducing LDI without prior LD, allowing a direct comparison of the combined method with conventional LDI – also for ambient aerosols and on the same instrument.

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175 **Table 1** Optical parameters and laser systems used in the experiments.

	Laser desorption		REMPI	LDI
Laser type, medium	Gas, CO_2	Solid-state, Er:YAG	Gas-Excimer, KrF	Gas-Excimer, KrF
Wavelength (nm)	10600	2940	248	248
Beam diameter (mm)	1 x 1 (Gaussian)	5 x 5 (Super-Gaussian/flat top)	5 x 10 (Gaussian x flat top)	0.2 x 0.4 (Gaussian x flat top)
Pulse energy (mJ)	15	160	4	4
Pulse duration	250 ns	200 µs	5 ns	5 ns
Peak irradiance (W cm^{-2})	1.5×10^7	3.2×10^3	1.6×10^6	1.0×10^9

3 Results and discussion

3.1. Two-step LD-REMPI for laboratory particles

First, we investigated the suitability of the Er:YAG laser for the LD-REMPI scheme (Fig. 1a) in laboratory experiments for three different PAH-containing particle types, named diesel soot particles, wood ash particles, and tar ball particles. The most
180 probable PAHs reflected in the mass spectra are listed in Table 2. Note that isomeric substances, e.g., phenanthrene vs. anthracene, cannot be distinguished. Figure 2a shows the sum PAH mass spectra of each 500 diesel soot particles, top panel with LD using the CO_2 laser and lower panel with the Er:YAG laser. The mass spectrometric patterns for both LD lasers are very similar, showing detailed PAH signatures with dominant parent PAHs of low molecular weight from the combustion process (Frenklach, 2002) and some alkylated species, partly consisting of residues from unburned fuel (Spencer et al., 2006;
185 Anders et al., 2023). Note, that the fragments are virtually unrecognizable, underscoring the soft nature of the LD-REMPI approach. The histograms on the right show the distribution of PAH signal intensities among the particles for the two lasers. The CO_2 laser produces very intense PAH mass spectra more frequently, while with the Er:YAG laser more particles with low to moderate signals are observed. This can be attributed to the laser spot geometry: The Er:YAG laser has a large spot and hits the particle with high probability but relatively low intensity, whereas the focused Gaussian profile of the CO_2 laser can result
190 in very high signal intensities when a particle is fully hit. However, the difference is rather moderate, also because of a comparable hit rate for both lasers: 38 % (49 %) of the optically detected particles produced a clear PAH spectrum in this LD-REMPI approach with the CO_2 laser (Er:YAG laser). It is also remarkable, that the signal intensities for the summed mass spectra of the same number of particles are comparable for both lasers, despite the very different laser intensities, durations, and wavelengths. The high degree of similarity can be explained by the underlying physical mechanisms of LD, where the
195 energy transferred to the particle eventually results in thermal desorption for laser pulses longer than a few picoseconds (Schmidt et al., 2023). In addition, saturation effects in the REMPI process might play a role (Gehm et al., 2018). The extent

of evaporation during LD cannot be determined from the experimental data. However, the broad size distribution (Fig. S1) and the high pulse-to-pulse variability (Fig. S2) suggest that complete vaporization of PAHs from the particles is unlikely. It is also important to note that in SPMS, due to the lack of quantitative measurement, minor differences in the mass spectra obtained do not undermine the applicability of the Er:YAG laser.

Table 2 Polycyclic aromatic hydrocarbons (PAHs) indicated by the measured mass spectra.

PAHs	m/z					
	Number of C in aliphatic side chains					
	0	1	2	3	4	5
Phenanthrene, anthracene	178	192	206	220	234	248
Pyrene, fluoranthene	202	216				
Chrysene(s), benzoanthracene(s), benzophenanthrene(s)	228	242	256	270	284	
Benzopyrene(s), benzofluranthene(s), perylene	252					
Benzo[g,h,i]perylene, indeno[1,2,3-c, d]pyrene	276					
	278					
Dibenzophenanthrenes(s), dibenzoanthracene(s)						
e.g. Coronen	300					
e.g. Dibenzopyrene(s)	302					
Important fragments	165, 189, 205, 219					

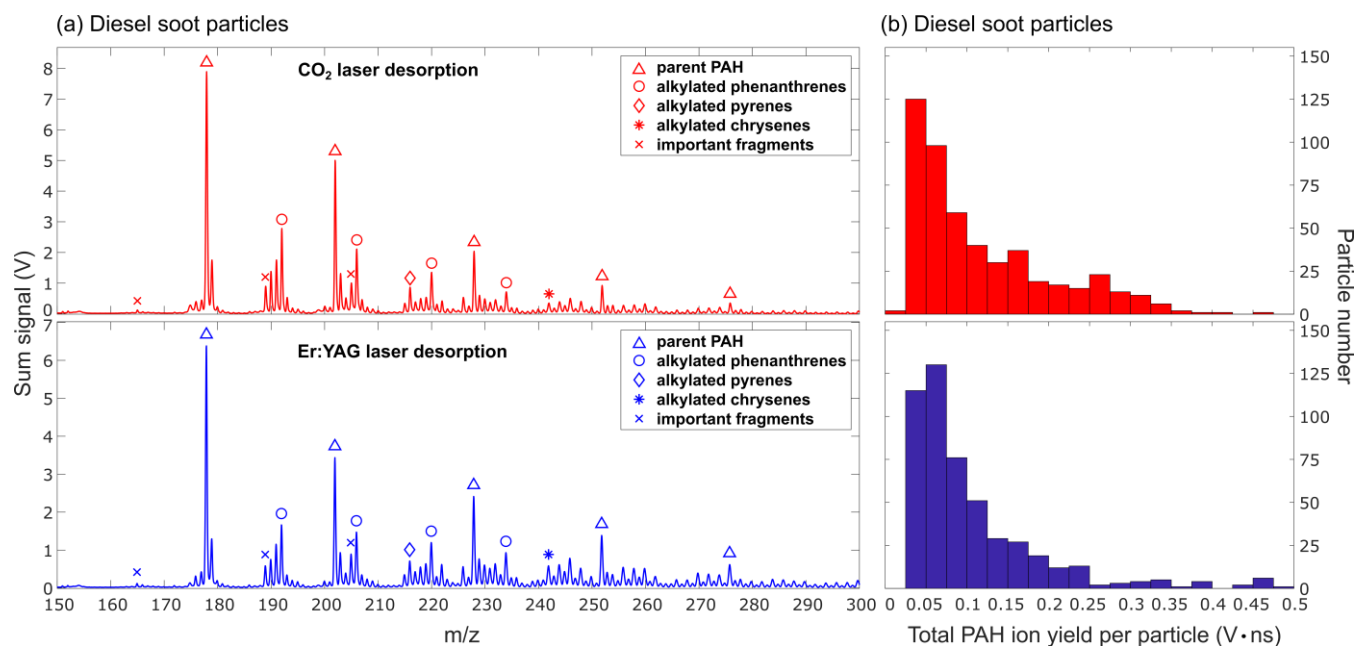



Figure 2 (a) The summed PAH mass spectra of 500 diesel soot particles, each, exhibit no significant differences when generated by LD-REMPI using a CO_2 laser (top) or the prototype Er:YAG laser (bottom) for the LD step. Note the very low fragmentation of the LD-REMPI method. **(b)** Histogram of the total PAH ion yield per particle. The CO_2 laser produces some more single-particle spectra with very strong PAH signals due to its high peak intensity in its Gaussian beam profile.

As a second representative particle type, wood ash particles were investigated. The results, including detailed PAH mass spectra and signal intensity histograms, are presented in the supplementary material (Fig. S3). In summary, the PAH profile differs significantly from diesel soot particles, with notable signals for the softwood combustion marker retene (m/z = 234) and higher-mass oxidized PAH molecules. These findings highlight the potential of single-particle PAH detection for source apportionment, especially in identifying combustion sources. Similar to the results with diesel soot particles, in a direct comparison between the CO_2 laser and the Er:YAG laser for LD, there are almost no differences in the mass spectra.

As a third type of model particle, tar ball particles were investigated, with detailed results presented in the supplementary material (Fig. S4). These particles serve as a simplified model for studying LD in organic aerosols from wood combustion, as they have comparable physical properties such as high viscosity, low volatility, and a brown color with high absorption in the UV-VIS due to their PAH content (Jacobson, 2012; Brege et al., 2021; Li et al., 2019). While no qualitative differences were observed in the PAH mass spectra between the CO_2 and Er:YAG lasers, the Er:YAG laser produced intense PAH spectra more frequently, probably due to resonant absorption by the O-H stretching vibration of the solvent methanol (Linstrom, 1997). The hit rates for these particles were 54 % (49 %) for the CO_2 laser (Er:YAG laser). Further details and mass spectra are available in Fig. S4.

3.2 Ambient air application of the Er:YAG-based laser desorption

As the laboratory experiments demonstrated the ability of the Er:YAG laser to efficiently desorb organics from different particle types, these results need to be validated in a field study for ambient aerosols. The experiments were conducted at the campus of the University of Eastern Finland in Kuopio, FI (*62.8891° N, 27.6290° E*) from March 1 to 3, 2024. Ambient air masses were sampled at a height of 10 meters above the ground. These air masses came mainly from the south, where the large forests and rural landscapes of Southern Finland and the Baltic States dominate. Backward trajectories were calculated using the HYSPLIT model with GFS 0.25° meteorological fields as the input file (http://www.ready.noaa.gov/HYSPLIT.php, last access: July 8, 2024, see Fig. S5). The average PM_{10} concentration in this winter time period was 4.0 µg m^{-3} and the average $PM_{2.5}$ concentration was 3.4 µg m^{-3} (weather station Kuopio Niirala, https://en.ilmatieteenlaitos.fi/download-observations, last access: July 8, 2024).

Out of 97,063 optically detected particles in 23 hours, 1,450 revealed PAH spectra, defined by the presence of at least five of the peaks listed in Tab. 2. The average mass spectra from a representative set of 500 PAH-containing particles, each, are compared in Fig. S6 and show a similar overall pattern for both desorption lasers and a comparable hit rate with slightly higher PAH signals and reduced fragmentation for the Er:YAG laser. As mentioned above, size information is only available at the ensemble average (Fig. S1), but not at the single-particle level.

Beyond performance parameters, these experiments on real-world aerosols should reveal whether different wavelengths and laser parameters affect the results on a single-particle basis. Therefore, the 500 PAH mass spectra from each laser were independently analyzed using the ART-2a clustering algorithm with a vigilance factor of 0.75, 20 iterations, and a learning rate of 0.05 (Sultana et al., 2017). After visual inspection and manual grouping of the 17 (11) ART-2a clusters for the CO_2 laser (Er:YAG laser), four main clusters remained, containing ≈ 95 % of the particles; see Fig. 3. The first three clusters in Fig. 3a and 3b show strong signals from parent PAHs, with distribution maxima at low molecular weight PAHs (LMW, cluster #1), high molecular weight PAHs (HMW, cluster #3), and dominant PAH peaks at m/z = 228 and 252 (cluster #2). Such distributions were previously associated with wood combustion aerosols in ambient air (Passig et al., 2022), and the dominant peaks for benzo[*a*]anthracenes/chrysene (*m/z* = 228) and benzopyrenes (*m/z* = 252) in cluster #2 are an indicator of a higher photochemical age of the particles (Miersch et al., 2019). Of note, not only the mass spectra but also the number of particles in each cluster are comparable for the two desorption lasers, emphasizing a high degree of similarity between the two desorption processes despite the different wavelengths. The primary difference between the two lasers is the higher fragmentation caused by the CO_2 laser, which leads to the formation of cluster #4, characterized by dominant fragments with odd m/z values, while the fourth cluster produced by the Er:YAG laser again shows parent PAHs as the strongest signals, but

with a different intensity distribution. The results in Fig. 3 indicate that the compact Er:YAG laser can replace the more

255   commonly used CO_2 lasers for single-particle LD also in ambient air studies.

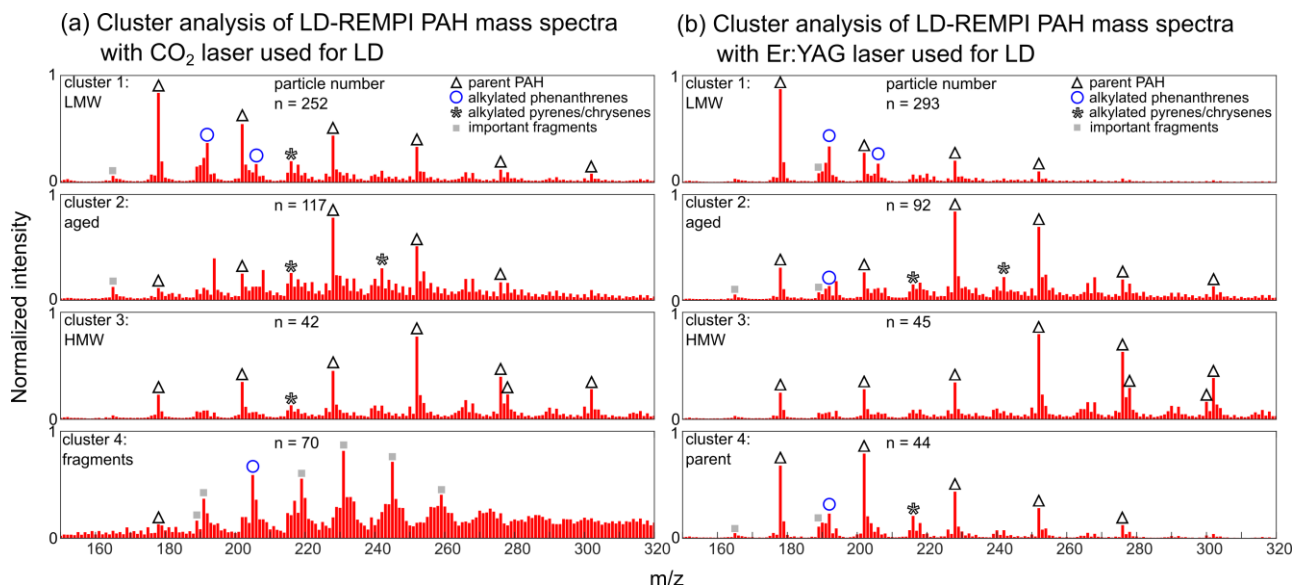



Figure 3 Main ART-2a clusters of each 500 PAH mass spectra from ambient air particles, exposed to **(a)** the CO_2 laser and **(b)** the Er:YAG laser for LD prior to REMPI. In the first three clusters, containing > 80 % of the particles, not only the mass spectral signatures are similar

260   but also the number of particles in the respective cluster. In the fourth cluster (< 14 % of the particles), significant differences are observed due to the higher fragmentation of the CO_2 laser, which can be explained by its beam profile and higher peak intensity.

3.3 Implementation in the combined ionization scheme for PAHs and inorganics – lab experiments

Recent developments using spatially and temporally tailored laser pulses allow the combined analysis of PAHs and inorganic particle constituents by simultaneously inducing REMPI of PAHs in the gaseous plume and LDI of the refractory particle

265   residue (Schade et al., 2019). We investigated the capability of LD by the Er:YAG laser for its implementation in this ionization technique for the same laboratory particles and for ambient air. The back reflection mirror was now used to allow the focused UV beam to be sent back into the ion source for LDI, as shown in Fig. 1b. In addition, the electronics have been modified so that the CO_2 laser and the Er:YAG laser are triggered alternately for LD of the first and second particles as before, and neither of them is triggered for the third particle. In the latter case, the unfocused UV beam does not induce REMPI because no gas

270   plume was previously formed, and the back-reflected UV beam only induces LDI, similar to conventional LDI-based SPMS. This allows a direct comparison of the PAH analysis using the combined ionization scheme with the Er:YAG and CO_2 lasers and with the conventional one-step LDI approach.

Figure 4 shows the results for soot particles, comparing LD with (panel a) the CO_2 laser, (panel b) the Er:YAG laser, and (panel c) one-pulse LDI only. The LDI part of the mass spectra (black and blue) are similar for all three methods, emphasizing

that the LD step has no significant effect on the LDI ion formation. For the PAH spectra in Fig. 4a and 4b, a slightly higher fragmentation can be noticed compared to the pure LD-REMPI results shown in Fig. 2. This is due to the back-reflected, narrow, high-intensity beam for LDI that cuts through a portion of the plume and fragments a fraction of the PAH molecules there. Of note, for the pure LDI process without prior LD, PAH signals are very weak and strongly interfered with molecular fragments (Fig. 4c).

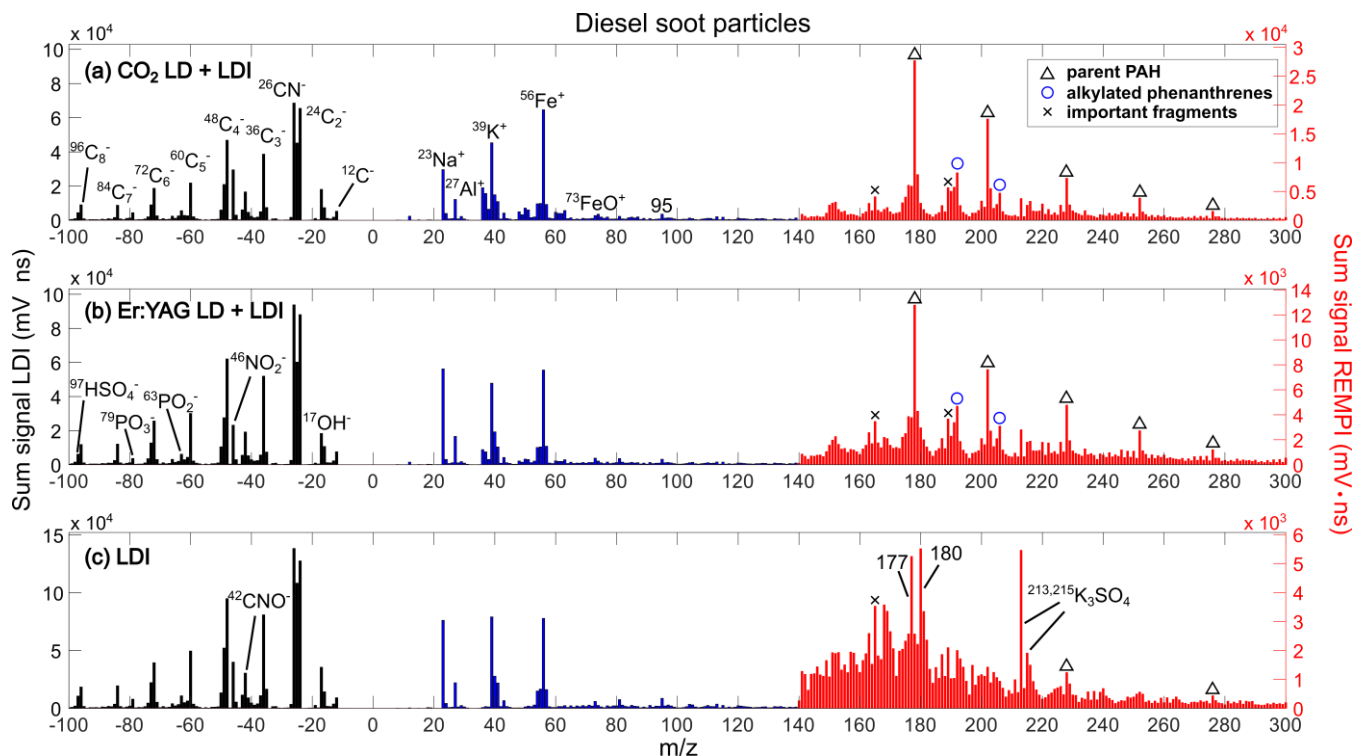



Figure 4 In the combined LD-REMPI/LDI scheme, PAH detection is combined with conventional inorganic characterization via LDI. Neither the PAH signature nor the LDI-derived composition is significantly affected when the CO_2 laser **(a)** is replaced by the Er:YAG laser **(b)** for the LD step. **(c)** In contrast, PAH signatures are barely detectable with conventional single-step LDI, n = 500 each.

For wood ash particles (Supplement, Fig. S7), LDI spectra show some minor differences of unknown origin, such as enhanced phosphate signals when the CO_2 laser was used for LD. Increased m/z = 178 signals can also be seen with the Er:YAG laser LD, probably due to slightly stronger absorption of phenanthrene/anthracene compared to other PAHs (Laurens et al., 2021). The wavelengths of the Er:YAG laser (3 µm) and the CO_2 laser (10.6 µm) lie at the respective edges of the PAH's IR absorption band, which could contribute to subtle differences in the mass spectral patterns. In contrast to diesel soot, PAHs are visible with LDI alone, but the combined LD-REMPI/LDI method amplifies the PAH signals by a factor of 5-8.

In the case of tar ball particles, the LDI mass spectra in Fig. 5a and 5b show similar fragmentation patterns. This indicates that resonant excitation of the OH-stretch vibration by the Er:YAG laser does not influence the subsequent LDI when investigating

organic aerosols. The PAH signatures are again comparable and approximately four times stronger than the one-step LDI process shown in panel c. Interestingly, the LDI mass spectra in panel c are different, showing stronger signals of soot and inorganic components. This points to the matrix effect of soot: only two types of real-world particles are capable of producing spectra with intact PAHs in one-step LDI: those with strong soot contributions (Zimmermann et al., 2003) and particles with dominant parent PAHs via so-called self-matrix ionization (Zhu et al., 2024). This underlines the superior and more universal PAH detection of two-step methods with LD-REMPI ionization, which is much less dependent on the particle matrix (Woods et al., 2001).

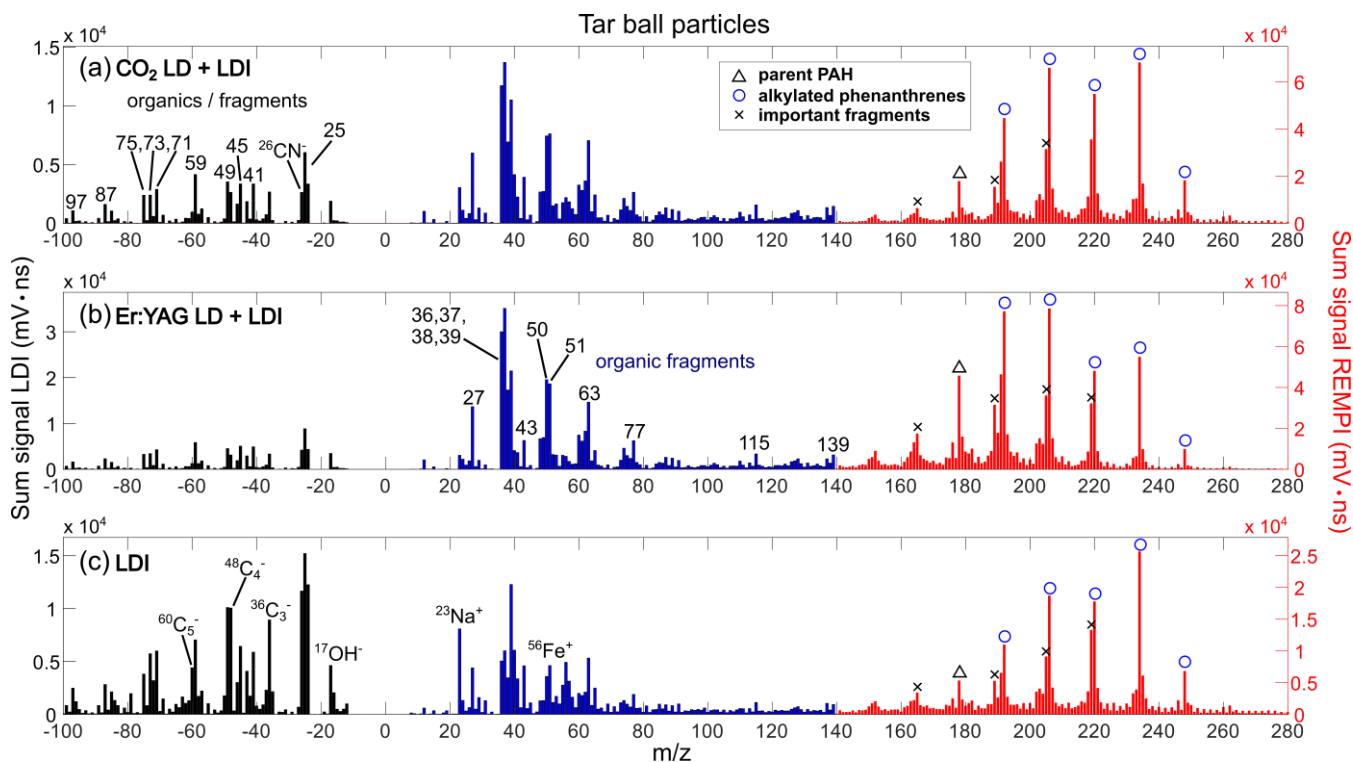



Figure 5 (a) and **(b)** Tar ball particles show comparable behavior in the combined LD-REMPI/LDI scheme, independent of the laser used for LD. **(c)** However, in single-step LDI, only particles with soot signatures and more pronounced signals from inorganics produce PAH mass spectra, underscoring the need for an UV-absorbing and ionization-enhancing matrix in LDI. This is reflected by the higher relative ion signals of soot clusters in panel (c). LDI anion signals are enhanced three times for better visibility, n = 500 each.

3.4 Implementation in the combined ionization scheme for PAHs and inorganics – ambient air experiments

In an extension of the ambient air experiments shown in Sect. 3.2, we continued the measurements for another 6 hours, now with the combined ionization scheme (Fig. 1b). Data analysis is more complex in this case because the signals from inorganics and PAH patterns should be analyzed separately (Passig et al., 2022). From 30,000 optically detected particles, 16,600 produced a cation LDI spectrum and 12,700 revealed bipolar LDI mass spectra, corresponding to a hit rate of about 55 %

(42 % bipolar; see Shen et al., 2024 for a comparison of hit rates for different LDI-based SPMS instruments). From these

310   particles, 1,846 showed additional PAH signatures as determined by the presence of at least five of the major PAH peaks listed in Tab. 2 (648 particles for the CO_2 laser, 644 for the Er:YAG laser, and 518 for LDI with the Excimer laser only). We selected 500 particles for each laser and analyzed their PAH pattern using ART-2a clustering; see Fig. S8 for the results. A detailed discussion of the particle ensemble is beyond the scope of this paper. In short, the PAH-containing particles were predominantly aged wood combustion particles with strong K^+ peaks and pronounced secondary sulfate and nitrate signals,

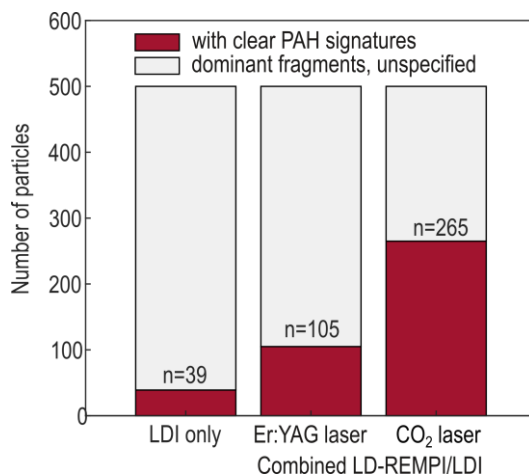
315   and sometimes soot signatures. Both the Er:YAG laser and the CO_2 laser produced comparable patterns of PAH mass spectra, however, with partly different numbers of particles in the respective classes (Fig. S8). For the LDI process only, without previous LD and REMPI ionization in the plume, the vast majority of the PAH mass spectra were dominated by fragments. This can be recognized more easily from Fig. 6, where the number of particles with dominant PAH peaks is illustrated for the three different laser excitation schemes.

320

Figure 6 In a direct comparison of ambient air aerosols, the combined LD-REMPI/LDI scheme yield PAH mass spectra with much higher efficiency compared to conventional LDI. In the experiments shown here, the prototype Er:YAG laser suffered from pulse-to-pulse instabilities. For a more stable Er:YAG laser, we expect a similar efficiency in detecting PAHs as for the CO_2 laser in the future. The high prevalence of stable parent PAHs and soot components favors the CO_2 laser and LDI compared to the Er:YAG laser. For some particle types,

325   PAHs are barely detectable with LDI; compare Fig. 4. The mass spectra and a cluster analysis are shown in the Supplement, Fig. S8.

Obviously, the Er:YAG laser was less efficient in producing clear PAH spectra than the CO_2 laser in this experiment. For a given particle type, achieving efficient plume expansion necessitates a specific laser energy threshold. When pulse energy fluctuations are significant, as for the prototype laser used here (refer to Supplementary Fig. S2), low pulse energies can result in inefficient plume expansion, thereby diminishing the hit rate and reducing signal intensities in the mass spectra – a problem

330   that will be solved with a more stable laser in the future. As noticeable from Fig. 6, the pure LDI process also produced some clean and evaluable spectra. Once again, it should be noted that these results are strongly dependent on the experimental conditions and particle type. It is well known that soot can act as an efficient matrix for PAH ionization in LDI, also in SPMS

(Zimmermann et al., 2003). Most of the PAH-containing particles detected here reveal also soot signatures by the presence of C_n- clusters in negative LDI spectra (Fig. S8), while in other field studies PAHs were mainly detected on organic carbon
335 particles without clear soot signatures (Passig et al., 2022). Parent PAHs, which are the dominant PAH species in the mass spectra observed here, are also particularly stable to fragmentation, allowing their analysis with LDI via self-matrix ionization (Zhu et al., 2024). In many other cases, other PAHs are important, such as alkylated phenanthrenes from incomplete combustion, which can indicate the particle source (Anders et al., 2023; Anders et al., 2024), or retene, which is a marker for coniferous wood combustion (Shen et al., 2012b). These PAHs are more susceptible to fragmentation than parent PAHs (Passig
340 et al., 2021; Gehm et al., 2018; Kruth et al., 2017) and could therefore be underrepresented in LDI. In the present data set, aromatics other than the parent PAHs are almost absent for all three laser excitation schemes, so a systematic comparison of the ratios of alkylated/parent PAHs is not possible. In previous tests in Central Europe at warmer temperatures of about 5–10 °C, only the combined two-step excitation scheme was able to detect PAHs in a similar comparison experiment with LDI (not shown due to technical difficulties with the SPMS system). In the experiment shown here, the weaker performance of the
345 Er:YAG laser compared to the CO_2 laser is probably a result of the large shot-to-shot variability of its pulse energy (see Fig. S2). It may also be related to the high abundance of parent PAHs that better resist the higher peak intensities of the CO_2 laser and the LDI laser beam. In general, the combined LD-REMPI/LDI scheme causes more fragmentation than the LD-REMPI approach alone, since part of the gas plume surrounding the particle is hit by the high-intensity LDI beam. Also, interferences between PAHs and inorganics occur more frequently, e.g., with $K_3SO_4^+$ at m/z = 213 and 215. However, it has the advantage
350 of detecting both inorganic components and PAHs of the same particle.

4 Conclusions and Outlook

We have directly compared a prototype solid-state laser with a more conventional CO_2 laser for laser desorption in two-step approaches for ionization in SPMS. Although the wavelengths (3 μm Er:YAG solid-state laser vs. 10.6 μm CO_2 laser) and pulse lengths (200 μs Er:YAG laser and 250 ns CO_2 laser) differ substantially, the resulting PAH mass spectra show a high
355 degree of similarity, and the hit rate is also approximately comparable. This can be explained by the desorption mechanism for laser pulses in the nanosecond to microsecond range, where the laser energy is eventually transferred to thermal energy and the organic material is ejected by thermal vaporization (Schmidt et al., 2023). Solid-state lasers have multiple advantages over gas lasers in terms of reliability, usability, and cost. In particular, the regular gas changes required for CO_2 lasers and the necessary provision of gas cylinders are avoided, which is of great importance for measurements in remote areas, on ships, or
360 in airplanes. This potential can be fully exploited if the excimer laser is also replaced by a (Nd:YAG) solid-state laser, making the two-step process much more flexible and easier to use. However, the large pulse-to-pulse variability of the current prototype Er:YAG laser needs to be overcome by developing a more stable system, and the maximum repetition rate should be increased

to allow measurements also in the unsynchronized "free-running" mode for ultrafine particles (Anders et al., 2023; Anders et al., 2024; Erdmann et al., 2005).

365   We also evaluated the advantages of the recently developed two-step approach with combined ionization for PAHs and inorganics (Schade et al., 2019) by direct comparison with conventional LDI method. The combined method clearly showed improvements in the detection of health and environmentally relevant PAHs by spatially separating the LD-REMPI and LDI processes. The technique facilitates detecting clear PAH signatures and inorganic/refractory particle components simultaneously. In addition to the higher detection rates for PAHs, we concluded that the combined technique is universally

370   applicable to mixed aerosols, which has been demonstrated previously (Passig et al., 2022; Anders et al., 2024), whereas conventional LDI is more limited to soot-containing particles (Zimmermann et al., 2003), pure PAH particles (Zhang et al., 2023), and could potentially introduce a bias toward parent PAHs. Furthermore, we have illustrated that the advantages of two-step processes extend beyond a specific type of desorption laser, as evidenced by comparing a solid-state Er:YAG laser with a CO_2-TEA laser.

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Data availability. Data are available on request from Johannes Passig (johannes.passig@uni-rostock.de).

Author contributions. M.S., H.H., and J.P. performed the SPMS experiments. M.S. and J.P. analyzed the data. T.K.B., L.A., A.K., and R.I. provided technical assistance. R.K. and N.G. constructed the Er:YAG laser. M.S. and J.P. wrote the manuscript. J.P. conceived the experiments. J.P. and R.Z. raised funding.

380   *Conflicts of Interest*. The authors declare no conflict of interest.

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