Ambient Single Particle Composition Measurement with Laser-Induced Breakdown Spectroscopy
PAAVO HEIKKILÄ

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ACADEMIC DISSERTATION
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ABSTRACT

Aerosol particles have a multitude of direct and indirect effects on human life and the planet. They cause millions of premature deaths annually, participate in the Earth’s water cycle through precipitation processes, affect the climate directly through absorption and scattering and indirectly acting as cloud condensation nuclei. Furthermore, the aerosol transmission of pathogens has been a cause célèbre since the unprecedentedly fast spreading of the latest coronavirus pandemic.

Measuring the composition of aerosol particles is essential to be able to append the knowledge on the factors affecting their toxicity and climate effects and to trace and monitor harmful particles and pathogens in the air. The particles in the local air may originate from a vast range of both nearby and remote sources and include a complex mixture of elements and molecules. Thus, in many applications, the composition must be measured on a single-particle level to maintain crucial information about the particles’ internal and external mixing state.

This thesis presents development toward a novel method capable of measuring the composition of aerosol particles on a single-particle basis utilizing laser-induced breakdown spectroscopy (LIBS). The technique utilizes efficient aerosol charging to enable electrodynamic focusing of particles sampled directly from the ambient air. The focusing is essential for maximizing the LIBS signal intensity acquired from individual particles. In the thesis, two novel aerosol charger designs are presented and characterized. The focusing efficiency with realistic charging states is thoroughly evaluated, and optical designs for LIBS analysis combined with the focusing systems are illustrated and characterized. Ultimately, a field-deployable instrument capable of analyzing the elemental composition of ambiently sampled aerosol particles on a single-particle basis is presented. The method’s ability to analyze multiple elements simultaneously from ambiently sampled single particles over a broad wavelength range and high resolution is unprecedented in aerosol technology.
ACKNOWLEDGEMENTS

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I have always felt welcome to ask and give help to my colleagues in the lab. Especially when I started to work in the aerosol physics laboratory as a summer student in the year of 2014 and many years afterwards, the help of other members of the lab has been vital to get into the track of research. I’d like to thank all the co-authors of the papers for their valuable inputs to the thesis process. Special thanks to Dr. Antti Rostedt for his valuable insights in many electrical and technical matters considering prototype development and building. Tuomas Seppä and Tommi Salo from the mechanical workshop are highly appreciated for the construction of many valuable prototypes used in the research.

My parents have built me a solid foundation in life, encouraging to curiosity and in believing that any obstacle can be overcome. For this I am forever grateful. My siblings gave me the privilege to practice patience and communication skills, which I value greatly. I thank my friends for taking my thoughts off work when needed. My wife and best friend Maria, thank you for your love and support. This would not have been possible without you. Special thanks to our son Alvar, you made it easier to finish the thesis in time.
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## SYMBOLS AND ABBREVIATIONS

Symbols, in the order of appearance:

- $E_k, E_i$: Energies of states $k$ and $i$
- $\hbar$: Planck’s constant
- $\nu$: Frequency of a photon
- $c$: Speed of light in vacuum
- $\lambda$: Wavelength of a photon
- $I$: Measured emission intensity of a transition line
- $N_s$: Number density of atoms
- $l$: Emission path length
- $g_k$: Degeneracy of an energy level
- $A_{ki}$: Transition probability from state $k$ to $i$
- $T$: Temperature
- $Q(T)$: Partition function
- $k_B$: Boltzmann constant
- $F$: Force acting on a particle
- $m$: Mass of a particle
- $a$: Acceleration of a particle
- $\eta$: Viscosity of a fluid
- $d_p$: Diameter of a particle
- $r$: Position of a particle
- $C_c$: Slip correction factor
- $q$: Total electric charge of a particle
- $E_{AC}$: Electric field strength due to AC potential
- $\omega$: Angular frequency
- $E_{DC}$: Electric field strength due to DC potential
- $g$: Gravitational acceleration
- $Z$: Dimensionless position of a particle
Position of a particle in an axis of interest  
Distance from an electrode to the focus spot of an EDB  
Dimensionless time  
Drag force parameter  
Electric force parameter  
Geometric constants describing the electric field in an EDB  
Number of elementary charges from diffusion charging  
Number of elementary charges from field charging  
Number of elementary charges  
Permittivity of free space  
Elementary charge  
Mean thermal velocity of ions  
Ion concentration  
Relative permittivity  
Electric field  
Electrical mobility of an ion  
AC-voltage applied to the electrodes of an EDB  
Electrical mobility of a particle  
Average position of a particle  
Initial position of a particle  
Effective relaxation time  
Mechanical mobility of a particle

Abbreviations, in alphabetical order:

AC
ALABAMA
APS
ATOFMS
ATD
BAMS
CMOS
CPC
CW

Alternating current  
Aircraft-based laser ablation aerosol mass spectrometer  
Aerodynamic particle sizer  
Aerosol time-of-flight mass spectrometry  
Arizona test dust  
Bioaerosol mass spectrometry  
Complementary metal oxide semiconductor  
Condensation particle counter  
Continuous wave
<table>
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<tr>
<th>Acronym</th>
<th>Description</th>
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<tr>
<td>DC</td>
<td>Direct current</td>
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<tr>
<td>DMA</td>
<td>Differential mobility analyzer</td>
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<td>EDB</td>
<td>Electrodynamic balance</td>
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<tr>
<td>HYSPLIT</td>
<td>Hybrid single-particle lagrangian integrated trajectory model</td>
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<tr>
<td>ICCD</td>
<td>Intensified charge-coupled device</td>
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<tr>
<td>IQR</td>
<td>Inter-quartile range</td>
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<tr>
<td>LAAPTOF</td>
<td>Laser ablation of aerosol particles time of flight mass spectrometer</td>
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<td>LAMPAS</td>
<td>Laser mass analyzer for particles in the airborne state</td>
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<td>LEQ</td>
<td>Linear electrodynamic quadrupole</td>
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<tr>
<td>LIBS</td>
<td>Laser-induced breakdown spectroscopy</td>
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<tr>
<td>LOD</td>
<td>Limit of detection</td>
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<td>MALDI-ATOF</td>
<td>Matrix-assisted laser desorption/ionization-time-of-flight mass spectrometry</td>
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<tr>
<td>NAMS</td>
<td>Nanoaerosol Mass Spectrometer</td>
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<tr>
<td>Nd:YAG</td>
<td>Neodymium-doped yttrium aluminum garnet</td>
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<tr>
<td>NIST</td>
<td>National Institute of Standards and Technology</td>
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<td>NOAA</td>
<td>National Oceanic and Atmospheric Administration</td>
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<td>PALMS</td>
<td>Particle analysis by laser mass spectrometry</td>
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<td>PhotonLIZA</td>
<td>Laser ionization aerosol mass spectrometer</td>
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<tr>
<td>PMT</td>
<td>Photomultiplier tube</td>
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<tr>
<td>SAAC</td>
<td>Size-amplification aided aerosol charger</td>
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<tr>
<td>SPAA</td>
<td>Spectroscopy platform for ambient aerosol analysis</td>
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<tr>
<td>SPAMS</td>
<td>Single particle aerosol mass spectrometry</td>
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<td>SPLAT</td>
<td>Single particle laser ablation time-of-flight mass spectrometer</td>
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<td>SPMS</td>
<td>Single particle aerosol mass spectrometry</td>
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<td>XRF</td>
<td>X-ray fluorescence</td>
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AUTHOR’S CONTRIBUTION

Paper 1  The author participated in planning the design of the novel aerosol charger and built and characterized it. The author conducted the simulations and calculations. The author participated in the planning and conducted the experiments and data processing presented in the paper, excluding the droplet-residual analysis. The author designed the parts relevant to aerosol analysis of the optical system. The author wrote the paper and the supplementary material with the help of the co-authors.

Paper 2  The author designed and built the optical system combined with the electrodynamic particle focusing. The author conducted the calculations and simulations. With the help of the co-authors, the author planned the experiments and data processing presented in the paper. The author wrote the paper and the supplementary material. All authors contributed to the planning phases and reviewing the paper.

Paper 3  The author designed and built the new optical system combined with the new electrodynamic particle focusing system. With the help of the co-authors, the author designed and built the field-deployable platform. The author planned and conducted the experiments and data processing presented in the paper. The author wrote the paper and the supplementary material. All authors contributed to the planning phases and reviewing the paper.
Ambient air contains a complex mixture of gases and particles. This mixture, an aerosol, has multitude direct and indirect effects on human wellbeing on an individual and planetary level. For example, particulate matter is estimated to be one of the main causes of excess mortality, with millions of premature deaths annually (Pozzer et al., 2023; Lelieveld et al., 2015). Furthermore, aerosol particles have a crucial role in the planetary water cycle by acting as droplet- and ice condensation nuclei in clouds (Riemer et al., 2019; Murray et al., 2012; DeMott et al., 2010; Petters and Kreidenweis, 2007). The aerosol-cloud dynamics are also directly linked to the radiative balance of the Earth, thus affecting the climate (Riemer et al., 2019, Vergara-Temprado et al., 2018). The unprecedentedly rapid spreading of COVID-19 pandemics was due to efficient spread of pathogen particles in the aerosol phase, transmitting the disease over long distances in indoor spaces (Y. Liu et al., 2020, Zhang et al., 2020).

A key component in understanding the effects of aerosol particles is their chemical composition (Riemer et al., 2019). When the chemical characteristics of toxic aerosols become more known, real-time monitoring of ambient aerosol’s elemental composition may help improve mitigating the adverse health effects in heavily polluted urban areas (Hopke et al., 2020). One of the major gaps in the knowledge about cloud dynamics is the lack of detailed experimental data on single particles acting as ice nuclei in clouds (Murray et al., 2021; Schmidt et al., 2017). Accurate single particle chemical composition measurements are being developed to be able to distinguish between airborne bioaerosols, showing promising results in future mitigation actions against pathogen spreading through the air (Lu et al., 2022; Li et al., 2023). In these cases, it is important to be able to resolve the chemical composition of particles on a single particle basis: Single particle analysis allows for particle classification, which is important in mitigating toxic particle emissions and distinguishing particle types that act as ice nuclei. Moreover, accurate single particle composition analysis is required in not only distinguishing between particle types but also between different bacterial cells, which is an important step towards pathogen spread mitigation.
The most established method to measure the composition of individual aerosol particles is single particle aerosol mass spectrometry (SPMS) (Riemer et al., 2019; Pratt and Prather 2012; W. D. Davis 1977). SPMS instruments are relatively expensive and strongly scientific, thus significant amount of the research with SPMS technology is conducted based on custom-built unique systems developed in different scientific institutions. Examples of such systems include ATOFMS (Prather et al., 1994), LAMPAS (Trimborn et al., 2000), SPLAT (Zelenyuk and Imre 2005), PALMS (Thomson et al., 2000) and ALABAMA (Brands et al., 2011). Furthermore, specialized SPMS systems for operation like bioaerosol research (MALDI-ATOF (Wuijckhuijse et al., 2005) and BAMS (Fergenson et al., 2004)) or nanoaerosol characterization (NAMS, S. Wang et al., 2006) have also been developed. A few commercial instruments also exist, namely SPAMS 3.0, (Livermore Instruments Inc.), LAAPTOF (ATL Lasertechnik GmbH), SPAMS (Guangzhou Hexin Instrument Co., Ltd), PhotonLIZA (Photonion GmbH) and ATOFMS (TSI Inc., discontinued). The acronyms are opened in the list of abbreviations. With SPMS, chemical composition up to molecular level can be measured in real time from particle sizes ranging from 10 nm to 10.0 µm, depending on the specific instrument in use. With SPMS, high analysis rates are also achievable, in the order of $10^3 – 10^6$ analyzed particles/day (Riemer et al., 2019). While merited with versatile possibilities, SPMS technology holds a few shortcomings, which include moderate quantitative analysis power and intricate data analysis, need for frequent calibration and high vacuum (X. Wang et al., 2023; Isokääntä et al., 2020; Zhu et al., 2020). Furthermore, the equipment is expensive and heavy.

As will be presented throughout this thesis, another possibility to measure ambient aerosol composition in real time is laser-induced breakdown spectroscopy (LIBS, Singh and Thakur, 2020; Cremers and Radziemski, 2013). LIBS is a relatively new spectroscopic method able to resolve nearly all elements of the periodic table with a multi-element capability within a single measurement. It utilizes a tightly focused laser pulse to turn material into plasma, which emits material-specific spectral emission as it cools down. The main problem in using LIBS to analyze ambient particles is the relative rarity of the particles compared to the volume that the signal originates from. As an order-of-magnitude calculation, if the optimum signal for aerosol analysis originates from a focal volume of $10000 \, \mu m^3$ and the aerosol number concentration is 1000 particles/cm$^3$, the probability to hit a particle is approximately 0.001 %.

Two approaches to solve the low hitting chance problem have been presented in prior literature for ambient aerosol analysis. The simplest and mostly documented
method is to use a high pulse laser energy combined with a fast repetition rate to increase the yield of successful spectra (Hettinger et al., 2006; Lithgow et al., 2004; Carranza et al., 2001). Another method is to utilize aerodynamic focusing of the particles with triggered pulse laser operation (Sipich et al., 2023; Maeng et al., 2017; Tjärnhage et al., 2013; Hybl et al., 2006). With the un-triggered method, larger pulse energies lead to larger sample volumes than in the example calculation, and the researchers have reached hit rates between 0.01 – 1 %. With the aerodynamic focusing and triggering of the pulse laser, hit rates above 50 % have been achieved. However, for both methods, without efficient focusing of the particle directly to the focus of the pulse laser, the particle is ablated due to plasma-particle interaction rather than laser-particle interaction, which leads to strongly diminished signal intensity (Järvinen and Toivonen 2016; Carranza and Hahn, 2002). Consequently, only four papers report the analysis of outdoors aerosol analysis with LIBS (Hybl et al., 2006; Hettinger et al., 2006; Lithgow et al., 2004; Carranza et al., 2001), and only one of them (Hybl et al., 2006) report wideband spectral analysis of single particles. Due to the low resolution of the measurements conducted by Hybl et al., only Na, Ca and K could be simultaneously detected from large supermicron particles, but it is an important study proving the potential of ambient multi-element measurements conducted with LIBS.

In the light of optimal emission signal reached with direct laser-particle interaction, the methods presented in the literature suffer from too inefficient particle focusing. Thus, earlier literature covers no LIBS measurement results from ambient aerosols that utilize a high-resolution broadband spectrometer, capable of dividing single particles into distinct categories based on their elemental composition. Instead, most of the earlier studies have been conducted with a narrow wavelength spectrometer connected to an ICCD camera. With such combination, high dynamic sensitivity is achieved at the cost of multi-element operation.

In this thesis, methods to efficiently focus individual particles for LIBS analysis are developed and characterized. Furthermore, a field-deployable platform to conduct the analysis in situ with a broadband spectral capability will be presented. The presented technique shows unprecedented performance and potential in analyzing and categorizing initially unknown aerosol particles from relevant concentrations of ambient air on a single-particle basis. The technology can be realized as lighter and cheaper instrumentation with less labor-intensive data processing compared to single-particle mass spectrometry.
1.1 Research questions and objectives

The core difficulty of analyzing aerosol particles with LIBS lies in the fact that the aerosol particles are rare distinct points in space and the optimal signal from LIBS analysis also emanates from a small volume. In comparison, this is analogous to trying to hit a baseball that is randomly located within a dark room of a thousand cubic meters. Figure 1 illustrates this problem.

![Figure 1. Illustration of the research objective of bringing the aerosol particles into the optimal emission volume. In (a), the pulse laser and the plasma miss the particle, leading to no emission signal. In (b), the pulse laser turns the gas into plasma, which then spreads into the particle, leading to weak signal. In (c), the laser directly interacts with the particle, leading to a strong emission signal.](image)

Due to aforementioned reasons, our approach holds a basic assumption that the particles must be efficiently focused prior to LIBS analysis. Exact particle focusing with an electrodynamic balance (EBD) combined with LIBS has been presented by Järvinen et al., (2014). and Saari et al., (2016) for individual droplet residual particles, which laid the foundation for the research in this thesis. Focusing droplet residuals via the EDB is a commonly used technique in aerosol science, as droplets are readily charged upon generation, which leads to efficient focusing (Kaur Kohli et al., 2023; E. J. Davis 2011; E. J. Davis and Ray 1980). Thus, our main research questions are, starting from a broader perspective and approaching the details:

- How to repeatably resolve single particle composition on a multi-element level with LIBS in a real-world environment?
• How to efficiently focus initially uncharged particles into the LIBS focal volume directly from the ambient air?

• How to acquire high enough charging state for electrodynamic focusing?

Directly linked to the research questions, the research objectives were:

• To build and characterize a particle focusing system based on electrodynamic focusing, efficient enough for direct laser-particle interaction in LIBS analysis.

• To combine the optical components of LIBS with the particle focusing system on an efficient manner, enabling single-particle classification through multi-element analysis.

• Ultimately, to build a field-deployable instrument for real-world applications based on the developed methods.

After this introduction, the basics of the used methodologies are presented, namely LIBS, electrodynamic focusing and aerosol charging (Chapter 2). This is followed by novel methods developed for efficient charging and focusing of ambiently sampled particles, and optical designs to combine LIBS analysis with the particle focusing (Chapter 3). In Chapter 4, performance of the multi-element analysis and particle classification is demonstrated and evaluated. Finally, the main outcomes and the significance of the research is discussed in the last chapter.
2 FUNDAMENTALS

The approach for the composition analysis of aerosol particles presented in this thesis is based on laser-induced breakdown spectroscopy combined with electrodynamic focusing. In this chapter, the theoretical background covering the fundamentals and relevant aspects considering the method are presented.

2.1 Laser-induced breakdown spectroscopy (LIBS)

In laser-induced breakdown spectroscopy (LIBS), an energetic laser pulse is focused on a sample, turning it into hot plasma consisting of free electrons, ions, molecules, and neutral elements. The latter three contain excited electrons in their atomic or molecular orbitals. As the plasma cools down, the electrons return to lower energy states, releasing their energy as photons. These emitted photons have energies corresponding to the difference between the energy states of the electrons, which is furthermore determined by the electron structure of the molecule or atom in the plasma. Recalling the relation between photon energy and wavelength:

\[ \Delta E = E_k - E_i = h \nu_{ki} = \frac{hc}{\lambda_{ki}}, \]  

by detecting the photons with different wavelengths, one can distinguish between elements, as each element has their own unique electron structure (Hollas 2004). In (1), \( E_k \) and \( E_i \) are the energies of the upper and lower energy states, \( h \) and \( c \) are the Planck constant and the speed of light, \( \nu_{ki} \) is the frequency and \( \lambda_{ki} \) is the wavelength of the emitted photon.

The basics of laser-induced plasma formation in gases has been extensively studied in the literature (Wu et al., 2016; Hahn and Panne 2007; Morgan 1975). Air breakdown may occur with local laser intensities in the order of \( 10^{10} \) W/cm\(^2\) and above. The breakdown intensity threshold is a function of laser wavelength, with shorter wavelengths leading to decreased threshold intensity (Wu et al., 2016). The breakdown is initiated by multiphoton ionization, in which two or more photons are simultaneously absorbed by an atom or a molecule, releasing a free electron. These
released electrons readily absorb more energy from the photons of the laser pulse, gaining energy and releasing more electrons as they collide with the surrounding matter. This process of electron avalanche ionization is witnessed as a visible spark of plasma generated in the focal region of the laser pulse. The wavelength dependency of the breakdown is caused by more efficient ionization by the more energetic photons, accelerating the initial free electron production into the gas.

In addition to each atom having unique electron structure, the electron transitions are dictated by the selection rules of quantum mechanics (Hollas 2004). Any transition from an energy state to another is not allowed but must follow basic quantum rules of atomic electron transitions. Selection rules further increase the flux of photons emitted by certain discrete photons, as the number of possible transitions is limited by them. Figure 2 (a) illustrates the first few transitions of an aluminum atom with the transitions observed in this work highlighted as thick lines (Kramida and Ralchenko, 1999). A part of an emission spectrum measured with LIBS from a single kaolinite particle is shown in Figure 2 (b), exhibiting the highlighted transitions.

Figure 2. Energy diagram of the first few energy states of aluminum and the allowed transitions between them (a), including an emission spectrum of the highlighted transitions (b). The emission spectrum originates from a 1 µm kaolinite particle.

The quantum numbers marked in Figure 2 (a) follow a spectroscopic notation described in detail in literature (Hollas 2004). Briefly, the horizontal thick lines represent an energy state, the s, p d (or S, P, D) are the azimuthal quantum number
the numbers before the lowercase letters are the main quantum number \( n \) and the subscript number after the capital letters are the total angular momentum quantum number \( j \). Some of the allowed transitions are drawn into the figure with dashed lines.

Due to element-specific electron structures and the selection rules, some transitions are more likely to happen during electron relaxation than others, leading to varying emission peak intensities (Thakur, 2007). This phenomenon is observable within a single element and between the elements. Statistical methods can be used to estimate the expected intensities and they can be compared to the measured ones to provide insight about the plasma parameters and relative concentrations of the elements in the sample. If the plasma is in local thermal equilibrium, then the distribution of electrons in the energy states follow the Boltzmann distribution (Hollas 2004; Ciucci et al., 1999). Furthermore, if the plasma is optically thin and has sufficient number of free electrons (Cristoforetti et al., 2013), the emission line intensity for a certain energy transition can be written as, derived from the Boltzmann distribution:

\[
I = N_s l \frac{hc}{\lambda_{ki}} g_k A_{ki} \exp \left( -\frac{E_k}{k_BT} \right). \tag{2}
\]

In (2), \( I \) is the emission intensity over a full solid angle, \( N_s \) and \( l \) are the number density and the path length of the emitting atoms, \( h \) and \( c \) are the Planck constant and the speed of light, \( \lambda_{ki} \) is the transition wavelength, \( g_k \) is the degeneracy of energy level \( k \), \( A_{ki} \) is the transition probability between states \( k \) and \( i \), \( T \) is the temperature and \( Q(T) \) is the partition function (Gornushkin et al., 2010; Ciucci et al., 1999). With simple algebra, Equation (2) can be rearranged and rewritten as the so-called Boltzmann plot equation:

\[
y = mx + d, \tag{3}
\]

in which

\[
y = \ln \left( \frac{l \lambda_{ki}}{g_k A_{ki}} \right), \quad x = E_k, \quad m = -\frac{1}{k_BT}, \quad d = \ln \left( \frac{chlN_s}{Q(T)} \right). \tag{4}
\]

In Equations (2) – (4), the \( E_k, g_k, A_{ki} \) and \( k_B \) are literature values. If the photon detection efficiency of different wavelengths is known or the transition wavelengths are spread into a sufficiently narrow band to approximate the efficiency as identical,
one can directly estimate the plasma temperature via curve fitting from the slope of Equation (3) (Völker and Gornushkin, 2022). Furthermore, by utilizing a combined Saha-Boltzmann equation, one can estimate the electron density of the plasma and the proportional concentrations of the main elements in the plasma without prior calibration (Gornushkin et al., 2010; Ciucci et al., 1999). An example Boltzmann plot is shown in Figure 20 in Section 4.2.

A basic LIBS system consists of a pulsed laser, focusing optics, emission collection optics, spectrometer, and a detector (Noll, 2012). Such a system is illustrated in Figure 3. For nanosecond pulse times, the used pulse energies are usually in the order of 1-100 mJ. With solid samples, the sample itself restricts the optical access to the sample, and thus the emission needs to be collected from the excitation hemisphere. As the plasma emits a strong background of bremsstrahlung, a common procedure is to wait for the plasma to cool slightly before starting the emission collection (Rai and Thakur, 2007).

![Figure 3. A schematic figure of a typical LIBS setup. A laser pulse is generated and focused into the sample, turning it into plasma. The emission is collected and guided into a spectrometer and a detector. The resolved emission spectrum provides insight into the composition of the sample.](image)

Aerosol particles can be considered especially suitable for LIBS analysis for several reasons. For aerosol particles, the emission can be collected from any direction, as the particles are essentially point-like, and don’t limit the usable dimensions for the optical system. Thus, the emission collection can be built to minimize the bremsstrahlung background from the plasma, enabling the use of minimal waiting times after the laser pulse. The quantitative analysis power of LIBS
also suffers from matrix effects for solid samples, leading to the need of recalibration based on the sample and matrix material (Takahashi and Thornton, 2017; Hahn and Omenetto, 2010). If the aerosol particles can be analyzed directly from the ambient air, the matrix is gaseous, which substantially decreases the matrix effects. Furthermore, the laser pulse energy requirement to ablate a whole particle in the size range below approximately 3 µm in diameter is in the order of a few millijoules (Järvinen and Toivonen, 2016). The option to operate in low energies leads to decreased background plasma radiation, less emission from the matrix gas and lighter requirements from the pulse laser hardware. An apparent limitation is that one particle can only be analyzed once, as it is fully evaporated during the analysis. Thus, a practice of averaging over multiple spectra acquired from the same sample cannot be used when analyzing initially unknown particles, as opposed to bulk analysis.

As mentioned in the introduction, the main problem utilizing LIBS in aerosol analysis is the difficulty in bringing the particles into the focus spot of the laser. Methods for electrodynamic focusing of individual particles are presented to overcome this problem in the following section.

### 2.2 Electrodynamic focusing of particles

Electrodynamic balances (EDB) have been used in aerosol science for decades to study the properties of aerosol particles (E. J. Davis, 1997; Wuerker et al., 1959; Millikan, 1913). In an EDB, symmetrical oscillating electric field is produced via an AC voltage set into symmetrical electrodes. This field would cause a charged particle to oscillate around the symmetry focus, and the viscous force caused by gas inside the EDB dampens the oscillation, leading to a net force towards the focus. The focusing allows to trap particles into an EDB for long periods of time. Furthermore, by adjusting a DC voltage between the electrodes, the position of the trapped particle can be accurately adjusted. Multiple EDB designs have been presented for enhanced stability and controllability of particles (Hart et al., 2015; Heinisch et al., 2009; E. J. Davis, 1997; Hartung and Avedisian 1992; Berg et al., 1970). Considering optical measurements like LIBS, adequate optical access to the focus point of the EDB is essential. Figure 4 presents two designs for electrodynamic focusing of particles, in which (a) is an enhanced double-ring EDB design with focusing in all 3 dimensions and (b) is a linear electrodynamic quadrupole (LEQ) with focusing in only 2 dimensions (Hart et al., 2015; Heinisch et al., 2009). In the EDB, a DC voltage between the electrodes is required to overcome gravity. In the LEQ, particles are
vertically flowing through the symmetry axis and the vertical positioning is only controlled with the airflow. Both example designs allow for sufficient optical access to the focus point for LIBS analysis.

**Figure 4.** Examples of electrodynamic focusing systems. (a) is a double-ring type electrodynamic balance (EDB), which focuses particles into a well-defined point in space. (b) is a linear electrodynamic quadrupole (LEQ), which focuses particles into a symmetry line of the electrodes.

Several researchers have studied the balancing stability of an EDB in a sophisticated manner (Aardahl et al., 1997; Hartung and Avedisian 1992; E. J. Davis 1985). In the following the basic principles of a particle in an EDB are presented with Newtonian mechanics. As stated by Newton’s second law, the sum of forces acting on a rigid body causes an accelerating motion:

\[ \Sigma F = ma. \]  

(5)

Applying the forces acting on the particle in an electrodynamic balance without external forces, (5) becomes:
\[- \frac{3\pi \eta d_p}{c_c} \frac{dr}{dt} + qE_{AC}(r) \cos(\omega t) + qE_{DC}(r) - mg = m \frac{d^2r}{dt^2}. \quad (6)\]

In (6), \(d_p\), \(m\), \(q\), and \(r\) are the diameter, mass, electrical charge, and the position of the particle, respectively. \(E_{AC}\) and \(E_{DC}\) are the electric field (amplitude) strengths caused by the AC and DC voltage applied to the electrodes, \(\eta\) is the viscosity of the gas, \(\omega\) is the angular frequency of the oscillating electric field and \(C_c\) is the Cunningham’s slip correction factor. When assumed that gravity and the force caused by \(E_{DC}\) are equal in magnitude, or, in the case of an LEQ, perpendicular to the focusing direction, (6) can be rearranged as:

\[m \frac{d^2r}{dt^2} - \frac{3\pi \eta d_p}{c_c} \frac{dr}{dt} + qE_{AC}(r) \cos(\omega t) = 0. \quad (7)\]

This equation can be reduced into single axis of interest \(z\), and rewritten with dimensionless variables \(Z = \frac{z}{z_0}\) and \(\tau = \frac{\omega t}{2}\), and parameters \(\delta = \frac{36\eta}{c_c \omega \rho d_p^2}\) and \(\beta = \frac{24C_1 qV_{AC}}{\omega^2 z_0^2 \rho \pi d_p^3}\). In \(\beta\), \(z_0\) is the distance from the closest edge of an electrode to the focus point, \(C_1\) is a geometrical constant affecting the slope of \(E_{AC}\), and \(V_{AC}\) is the amplitude of the AC-voltage applied to the electrodes (Paper 2). Using the parametrization, one can write a generalized equation for the particle in an electrodynamic balance (E. J. Davis 2011):

\[\frac{d^2Z}{dt^2} + \delta \frac{dZ}{dt} + 2\beta Z \cos(2\tau) = 0. \quad (8)\]

Using Equation (8), the trajectory of a particle in an EDB can be numerically simulated. Utilizing simulations, stability ranges with respect to \(\delta\) and \(\beta\) can be recognized for a particle in an EDB. Figure 5 includes calculations of the stability ranges as presented by multiple prior authors (e.g. E. J. Davis 2011; Hartung and Avedisian 1992; E. J. Davis 1985), and a few example particles. The parameters for the particles have been calculated assuming that they are spherical water droplets with the maximum charge before coulombic fission, defined by the Rayleigh charge limit (Duft et al., 2003; Rayleigh, 1882). Furthermore, the constants \(z_0\), \(V_{AC}\), \(C_1\) and \(\omega\) defining the EDB have been set to equal the realistic dimensions and parameters used to operate the LEQ presented in Paper 3.
Figure 5. An example figure of the stability areas calculated with numerical simulations of Equation (8). The crosses represent example particles with a charge number defined by the Rayleigh limit focused with a LEQ presented in Paper 3. Figure modified from Paper 1.

Traditionally, the instability is caused by too strong electrical interaction between the electric field and the particle, leading to violent oscillation and eventually the particle depositing to one of the electrodes (E. J. Davis 2011). As the EDB is often used with large particles ($d_p > 5 \mu m$) generated by droplet dispensers with induction charging, the instability issue can be caused by too high electrical charge of them (Kaur Kohli et al., 2023). However, interpreting Figure 5, it can be readily observed that even if small particles ($d_p < 5 \mu m$) are in the maximum charge limit, their trajectory in our focusing system remains stable. It was readily observed that for particles in this size range combined with traditional unipolar aerosol chargers and the used electrode configurations, it is the lack of charge that causes issues, rather than excess thereof. Even though the trajectory is considered “stable” in the case of traditional analysis and violent oscillations don’t occur, efficient focusing won’t happen if the electric interaction is too small. Instead, the particles stay within the trap but do not reach the focus spot. Similar observation was made by Aardahl et al., (1997). Indeed, when combining initially neutral small particles with traditional aerosol chargers, the final charge is impossible to rise to a level to enable sufficient focusing power. Therefore, two novel aerosol chargers were employed to achieve adequate focusing efficiency, as presented in Chapter 3. The following section
provides details on the electrical charging mechanisms of aerosol particles, which aids in the design of an efficient aerosol charger.

2.3 Electrical charge of particles

The charging state of aerosols can be manipulated in several ways. If the aerosols are generated via droplet generation, charges in the Rayleigh limit can be readily obtained with the aid of an induction electrode (Kaur Kohli et al., 2023; Järvinen et al., 2014). Furthermore, utilizing radioactive or X-ray sources, an excess number of bipolar ions can be generated into gas, bringing an unknown aerosols’ charging state to a well-defined equilibrium (Tigges et al., 2015; Wiedensohler 1988; Fuchs 1963). To provide a unipolar charging state to ambient aerosol particles, the most established way is to utilize a corona discharge (Rostedt 2018; Dhaniyala et al., 2011). When a high voltage is applied to a conductive wire or a needle, the charge starts to accumulate to its periphery as it cancels the electric field inside the conductive material. With a high enough voltage, the localized high charge causes a strong electric field in its proximity, exceeding the breakdown of the ambient gas, generating ions. As the aerosol particles are exposed to the ion-laden gas, the ions attach to the particles and the particles acquire a net charge (Hinds 1999). Traditionally in corona chargers the electric current is in the order of 1-10 µA and a positive voltage is applied in the order of 1-5 kV to the discharge source (Ntziachristos et al., 2004; D. Park et al., 2007). The material of the discharge source is usually tungsten, as it has the best chemical resistance for the harsh conditions of the corona (Cogollo De Cádiz 2021).

Ion attachment to a particle may occur via two main pathways: diffusion charging, in which the ions reach a particle via Brownian motion, and field charging, in which an external electric field drives the ions towards the particle (Hinds 1999). Most electrical aerosol measurement methods are based on diffusion charging, as it is extensively documented and the dominant charging process for particles below a few hundred nanometers in size (Dhaniyala et al., 2011). Furthermore, as the particle size gets smaller, optical detection becomes increasingly difficult (Sorensen et al., 2011). With diffusion charging, usually charge numbers below 100 elementary particles per particle are achieved (Rostedt 2018). However, the primary goal of a diffusion charger is usually not to maximize the charge number, but to minimize particle losses and ensure good repeatability.
In the presence of a strong external electric field, the dominant charging process for particles above 1 µm in diameter is field charging. An external electric field accelerates ions into high velocities and thus enhances their accumulation into a particle. Furthermore, a large particle placed into an external field distorts it, causing the field lines to intersect with the particle (White 1951). This further enhances the charge accumulation, as free ions are (on average) moving along the field lines. The final charge acquired via field charging can be approximated as:

\[ n_f = \frac{3\varepsilon}{\varepsilon+2} \left( \frac{E\pi\varepsilon_0 d_p^2}{e} \right) \left( \frac{\pi e Z_i N_i t}{4\pi\varepsilon_0 + \pi e Z_i N_i t} \right). \]  

(9)

In Equation (9), \( n_f \) is the final charge number, \( d_p \) and \( \varepsilon \) are the diameter and the relative permittivity of the particle, and \( E \) is the electric field strength in the charging zone. \( \varepsilon_0, e \) and \( Z_i \) are the permittivity of vacuum, unit charge, and ion electrical mobility. \( N_i \) and \( t \) are the ion concentration and the time spent within the ions (Hinds 1999).

In Equation (9), the final charge is directly proportional to the electric field strength and to the square of the particle diameter. The first is due to the force driving the ions towards the particle and the latter due to particle cross-section being impacted by the ions in the electric field. Furthermore, increasing relative permittivity has an increasing effect on the charge due to a stronger distortion effect on the field lines. The last term of Equation (9) approaches unity as the product between time and ion concentration approaches infinity. In this situation, the high electric charge acquired by the particle causes the external electric flux to fully bypass it, and no more charge is accumulated to the particle. Then, Equation (9) may be approximated as the saturation charge:

\[ n_s = \frac{3\varepsilon}{\varepsilon+2} \left( \frac{E\pi\varepsilon_0 d_p^2}{e} \right), \]  

(10)

which estimates the maximum attainable charge when field charging is the dominant charging process. Figure 6 includes an illustration of the field lines with respect to a particle in saturation charge for different particle sizes and external field strengths. With a high ion number concentration, charge number close to the saturation charge may be attained in timescales under 1 s (Paper 1).
Figure 6. An illustration of a particle with the saturation charge in an external electric field. An increase in particle size (left to right) or electric field (up to down) causes an increase in the saturation charge.

Utilizing field charging, charge numbers of over 1000 charges/particle are achievable for supermicron particles (Papers 1 and 2; Smith et al., 1978; Hewitt 1957). To maximize the saturation charge, the external electric field should be close to the electric breakdown limit of the carrier gas, i.e. in the order of 1 kV/mm (Paper 1, Dhaniyala et al., 2011; Hewitt 1957). However, high external electric field combined with particles bearing a substantial charge often results in significant particle losses.
3 DEVELOPMENT OF EFFICIENT PARTICLE FOCUSING METHODS FOR LIBS ANALYSIS

Efficient focusing in an EDB or a LEQ is crucial to be able to hit the particles with the LIBS pulse laser in a repeatable manner. As discussed in Section 2.2, the major cause of focusing inefficiency for ambiently sampled particles is the lack of electrical charge. Therefore, two novel aerosol chargers were developed to maximize it. The first, presented in Paper 1, is based on enhanced field charging and is combined with the EDB, and the latter, presented in Paper 2, employs condensation growth of particles prior to charging and is combined with the LEQ. Both chargers were characterized in terms of achieved charging state, and the results are presented in Section 3.1. Using numerical simulations and the results from charging state measurements, the focusing efficiencies of the EDB and LEQ were evaluated, as presented in Section 3.2. In the third section, optical designs for LIBS analysis combined with the aerosol focusing systems are presented. Finally, Section 3.4 presents a field-deployable system built based on the optical design presented in Paper 3.

3.1 Increasing the electric charge of particles

The charger characterization methods are presented in more detail in Papers 1 and 2 and in the Supplementary Information of Paper 1. The presented particle sizes refer to the mobility diameter selected with a differential mobility analyzer (DMA) and the used particle material was dioctyl sebacate. The field-charging enhanced aerosol charger is presented in Paper 1 and Figure 7 (a). The charger consists of two concentric tubes with inner diameters of 2.0 mm and 13 mm. The corona discharge tip is connected to the end of the inner tube, from which the aerosol flows into the charging region. Thus, the particles are charged under the influence of the same strong electric field that invokes the corona discharge in the charger. With numerical simulations, the electric field strength was estimated to be in the order of $10^5 – 10^6 \text{ Vm}^{-1}$ in the charging region. A schematic figure of the charger and the achieved charging states are presented in Figure 7 (a) and (b). The inner tube of the charger is
in high potential, but due to symmetry, the particles experience minimal electric field inside the tube. However, by comparing the particle throughput with and without the corona discharge, the electrical losses of the charger were found to be about 50% for 1 µm sized particles. They are most likely caused by the high charging state and the strong electric field inside the outer tube after the corona discharge.

**Figure 7.** A schematic figure of the charger presented in Paper 1 (a). In the charger, aerosol flows through the inner tube, set to high potential. The corona discharge is at the end of the tube, enabling a high electric field during the charging process. The charge numbers acquired with the charger are presented in (b), combined with a fit to the charging mechanisms. Literature values are presented as comparison. Adapted from Paper 1.

From Figure 7 (b), one can see that the achieved charging states are in the order of 100 charges per particle for ca. 1 µm particles and exceed 1000 charges per particle for over 3 µm particles. As presented in Paper 1, the charge distribution is almost log-normal, and thus the arithmetic mean is somewhat larger than the geometric mean. The geometric mean is a better estimator of the charging state for the whole aerosol population, as the arithmetic mean overestimates the charging value for most of the particles due to the skewed nature of log-normal distributions. A comparison to literature values is also presented in Figure 7 (b) (Unger et al., 2004; B. Liu and Pui 1977; Hewitt 1957).

The charger design presented in Paper 2 and Figure 8 (a) includes the same field charger as in Paper 1, but the field charging is enhanced by condensation growth of particles prior to charging. The condensation growth is based on water supersaturation leading to water condensation to the particles, implemented via a
growth unit described in more detail by Hering and Stolzenburg (2005). The final size after the condensation growth was measured with an aerodynamic particle sizer (APS 3321, TSI Inc.) to be approximately 3 µm. As shown in Figure 8 (b), the size-amplified particles acquire more than 1000 elementary charges per particle in the field charger, which is roughly an order of magnitude more than without the size amplification. The size amplification aided aerosol charger (SAAC) is a breakthrough method to charge initially neutral sub-micrometer particles into high charging states. It enables the trapping and efficient particle focusing in EDB and LEQ systems for ambiently sampled particles, removing the need for artificial aerosol generation.

![Figure 8](image)

**Figure 8.** A schematic figure of the Size-Amplification Aided aerosol Charger (SAAC) (a), and charge numbers acquired with it (b). Condensation growth prior to particle charging enables for efficient field charging, and the final charge is thus about an order of magnitude higher than without size amplification. Panel (b) modified from Paper 2.

During the research towards Paper 2, it was noticed that with a positive polarity, the charger generates highly charged tungsten particles into the aerosol. Thus, the polarity was changed into negative. Furthermore, in Paper 2, the charger was used in a constant current mode rather than constant voltage mode, used in Paper 1. These modifications are seen as difference between the ungrown charging states between the results of the acquired charging states between Papers 1 and 2.

The next section presents the main results on the focusing efficiency and limitations of the EDB and of the LEQ, studied in Papers 1 and 2. The results are interconnected to both chargers and the charging states acquired by them.
3.2 Electrodynamic focusing efficiency and limitations

The electrodynamic focusing efficiency of the EDB and of the LEQ was modelled using electric field simulations combined with numerical differential equation solving of Equations (6) and (8). The simulations are presented in more detail in Papers 1 and 2, including their supplementary materials. For the EDB, which balances the particle in all 3 dimensions, it was found out that the field caused by the DC-voltage overcoming the gravitational force causes major instability to the balancing. For particles with relatively low charge, the DC voltage must be larger to overcome the gravitational force, compared to droplet residuals with a high charge. Furthermore, for ambiently charged particles, the focusing force caused by the AC-field is weaker. Thus, with too low charge, the relation between the forces caused by the AC- and DC- fields is in favor of the instability-causing DC-field. Utilizing Equation (6) and electric field simulations, the particle trajectory in an EDB was simulated with varying parameters of realistic particle charge numbers and sizes. A threshold AC-voltage applied to the electrodes leading to stable trapping was found to be:

\[ V_{AC}^* = \frac{z_0}{z_m c_1} \sqrt{\frac{3g z_i c_2}{2c_0}}. \]  

(11)

In (11), \( V_{AC}^* \) is the threshold voltage for successful particle trapping, \( z_0, c_0, c_1, c_2 \) are geometrical constants defining the EDB, \( z_i \) is the initial distance of the particle from the focus spot and \( Z_m \) is the electrical mobility of the particle. Interpreting Equation (11), one might conclude that if the particle is brought at the exact focus spot, there is no need for the AC-field, as every force ideally cancels each other. In reality this is not the case, as convection flows and unidealities in the geometry cause the particle to drift away from the focus with too low voltages, even if the threshold of Equation (11) is fulfilled. It was experimentally verified that for the used electrode configuration, an AC-voltage required to bring the particle from approximately 0.7 mm displacement is sufficient to stably keep the particle in the focus spot even with the disturbances affecting the balance. This observation was used in combination with Equation (11) to find the minimum charge values required for stable particle trapping. Figure 9 (b) shows these results calculated with AC-voltages of 1, 2 and 4 kV, the charge numbers presented in Section 3.1, and for particles with a charge defined by the Rayleigh limit. The electrode configuration of the used EDB is presented in Figure 9 (a) (Heinisch et al., 2009).
The dimensions of the used EDB trap (a) and threshold charge numbers required for stable particle trapping (b). The inner electrodes of (a) include the AC- and DC-voltages and the outer electrodes are set to ground potential. In (b), threshold charge numbers for stable trapping are presented as the solid lines for AC-voltages of 1, 2 and 4 kV, calculated from Equation (11). The DC-field is assumed to overcome gravity and the markers represent charge values acquired with the 2 different chargers presented in Section 3.1. Panel (b) modified from Paper 1.

From Figure 9 (b), one can observe that utilizing the field charger presented in Paper 1, the minimum particle size that can be repeatedly trapped from the ambient air is in the supermicron range for AC-voltages of 1-2 kV. Utilizing the SAAC, any ambient particles can be assumed to be stably trapped even with a lower voltage, as the charge numbers provided by it are far in the stable zone of Figure 9 (b). Nonetheless, for LIBS analysis, it is sufficient if the particle slowly drifts through the focus spot instead of stably trapping. However, this requires active manipulation of the DC-voltage to drive the particle through the focus, which slows and complicates the automatization of the system. Another challenge in utilizing the EDB in LIBS analysis is the high probability of multiple particles getting trapped simultaneously. As the flow through the system must be stopped whenever particle is trapped, the concentration must be correct to minimize multiple particle trapping and maximize single particle trapping. The benefit of using EDB for ambiently trapped particles is that the particle can be held in the trap over long periods of time. This enables to study different environment effects to the particle and utilize multiple non-destructive measurements such as fluorescence or Raman measurement before analyzing the particle with LIBS (Saari et al., 2016; Vehring et al., 1998).
To reach a more autonomous operation for LIBS analysis, the feasibility of a flow-through linear electrodynamic quadrupole (LEQ) was studied in Paper 2. In an LEQ, no DC-field is applied to overcome gravity, as the focusing is conducted in only 2 dimensions leaving gravity parallel to the flow. Utilizing Equation (6), electric field simulations of the LEQ and numerical differential equation solving, the average position of a single particle was found to follow the form:

\[ r(t) = r_0 \exp \left(-\frac{t}{\tau_{ef}}\right). \]  

In (12), \( r(t) \) and \( r_0 \) are the final and initial positions of the particle, \( t \) is time and \( \tau_{ef} \) is the effective relaxation time, which defines the drifting speed of the particle towards the focus spot. With a multitude of trajectory simulations with varying parameters in Equation (6), the relaxation time was found to be of the form:

\[ \tau_{ef} = \left(1 + m^2 B^2 \omega^2 \right) \left(\frac{z_0^4}{2m B Z^2 C_1^2 V_{AC}^2}\right). \]  

In (13), \( \tau_{ef} \) is the relaxation time, \( m, B \) and \( Z \) are the mass, mechanical mobility and electrical mobility of the particle, \( z_0 \) and \( C_1 \) are geometrical constants describing the LEQ (or EDB) and \( V_{AC} \) is the AC-voltage applied to the electrodes. As mentioned, in the LEQ, no DC voltage is applied to the electrodes, as gravity is parallel to the flow. Thus, it has no effect causing instability to the focusing. However, utilizing Equation (13) and experimental observations, it became quickly evident that utilizing corona charging only, the focusing power is not sufficient to drive sub-micrometer particles close enough to the symmetry line of the LEQ within a reasonable time. Thus, the SAAC was developed to minimize the relaxation time, as it is a strong function of particle charge: The electrical mobility, which is directly proportional to particle charge, is squared in the denominator. Thus, the relaxation time is inversely proportional to the square of the particle charge.

With low laser pulse energies, the optimal signal from a single particle originates within a radius of approximately 20 µm from the LIBS laser focus spot (Järvinen and Toivonen, 2016). Hence, Equations (12) and (13) were utilized in combination with the charging states acquired with the field charger of Paper 1 and the SAAC to estimate the time it takes for a particle to drift to within 20 µm radius from the LEQ symmetry line. The results of these calculations are shown in Figure 10 (b) as a function of particle diameter, along with example particles with charges of 2000, 4000 and 8000 elementary charges. Figure 10 (b) also includes a horizontal line to
clarify the one-minute mark, which is considered a reasonable relaxation time considering the flow velocity (a few mm/s) in the chamber. The constants $z_0$ and $C_1$ were acquired from the geometry of the LEQ and electric field simulations and the particles were assumed to be spheres with unit density. Figure 10 (a) illustrates the electrode configuration of the LEQ.

![Figure 10](image)

**Figure 10.** The dimensions of the LEQ used in Paper 2 (a) and relaxation times for different charging states as a function of particle diameter (b). Without size amplification, the relaxation time for submicron particles can be expected to be too long for adequate particle focusing. With the SAAC, the relaxation times are in the order of 10 seconds, which is sufficient for effective focusing in the LEQ. Panel (b) modified from Paper 2.

In line with experimental observations, Figure 10 (b) illustrates that the charging states acquired with the corona charger only are not sufficient for reasonable waiting times for small particle focusing. However, for particles above a few micrometers in size, the size amplification is not required. With the SAAC, the focusing is efficient in the sub-micrometer particle size range as well, even slightly increasing for smaller particles, as their electrical mobility increases more after the water is evaporated.

In the next section optical designs combined with the focusing methods are presented. As discussed earlier, the focusing was conducted with an EDB in Paper 1 and with a LEQ in Papers 2 and 3. Thus, the optical designs vary between the papers.
3.3 Combining optics to electrodynamic focusing

The particle focusing system and optical design were constantly developed during the research, and thus each paper includes slightly different configurations. The systems in Papers 1 and 2 were built on a static optical table for basic methodology research and the system in Paper 3 was built on a field-deployable platform to reach portability. Figures 11, 12 and 13 present the optical schemes of each system.

In Paper 1, the aerosol was focused utilizing an EDB presented in Figure 9 (a). The optics were built around a hexagonal chamber including a one-inch window on each side. The focusing area was illuminated by a 532 continuous wave (CW) laser introduced to the chamber through the ring electrodes and the particles were monitored using a CMOS-camera. The aerosol was introduced into the chamber from an inlet through one of the side windows. The emission was collected and focused into a spectrometer utilizing two achromatic doublet lenses (f = 50 mm & 100 mm) and the spectra were detected utilizing an ICCD camera. The optical design is presented in Figure 11 and a more detailed description of the system is available in Paper 1.

Figure 11. The optical design of Paper 1. As the focusing was conducted via an EDB, the optics were built on a hexagonal chamber to maximize access to the focus spot. The aerosol was introduced into the chamber from an inlet through one of the windows. The emission was collected with two doublet lenses and focused directly into the spectrometer. A CW laser was used to illuminate the focus spot through a window below the chamber.
With the EDB-LIBS system, we were able to show that trapping ambient, initially uncharged particles directly from the aerosol phase is possible. Furthermore, we were able to show that there is a clear benefit in operating the EDB in ambient mode rather than with particles generated from water, as the same test aerosol (kaolinite) showed significant emission of calcium in the wet-generated particles, which was diminished in the initially dry particles, as illustrated in Figure 16. A maximum sampling rate of 1 particle/minute was accomplished when analyzing generated kaolinite particles. The slow analysis speed and manual operation were the main drivers to strive towards a faster and more automated technique.

The optical system combined with the LEQ focusing used in Paper 2 is presented in Figure 12. As the LEQ rods shade the corners of the optical access to the focus line, the optics were to be built into a square, rather than hexagonal, geometry. The chamber was also lengthened into the vertical dimension to increase residence time. Increased residence time allows for the particles to efficiently drift to the focus line, as shown by Equation (13) and in Figure 10 (b). The aerosol was introduced from the top along the quadrupole axis, surrounded by a dry sheath air flow to ensure full evaporation of the particles and to somewhat suppress the diverging of the aerosol flow. The flows were approximately 0.1 and 0.3 lpm, respectively, leading to RH values below 30 %. The chamber was operated in room temperature.

In the design, an additional CW laser was introduced into the chamber to trigger the LIBS pulse laser operation: The laser was focused into the same focus spot as the pulse laser via a dichroic mirror and the scattering was monitored by a photomultiplier tube. As a particle was detected from the scattering, a signal from the photomultiplier tube (PMT) was acquired to trigger the pulse laser. A dichroic mirror was utilized to align the lasers into the same optical path. The emission was collected with a similar scheme as presented in the previous setup. Due to the decreased optical access to the chamber, a beam splitter was used between the CMOS camera monitoring the particle focusing and the PMT utilized for pulse triggering. More details about the setup are available from Paper 2.
Figure 12. The optical setup of Paper 2. The aerosol was focused with a LEQ and LIBS was triggered with the use of a photomultiplier tube (PMT). The scattering from the 405 CW laser(s) was split into the CMOS camera and the PMT using a beam splitter. The plasma was collected with two singlet lenses and directly focused into the spectrometer.

With the design of Paper 2, analysis rates of about 10 particles/minute were achieved for 300 nm NaCl particles, as presented in Figure 17. The development of the SAAC was shown to enable repeatable LIBS analysis of sub-micrometer particles. Thus, the autonomous operation of the SAAC-LEQ-LIBS combination was proven to function on a proof-of-concept level. The optical design left room for improvement, as the optics are arranged quadratically into a single plane, which decreases the optical access to the focus spot compared to the hexagonal structure. Furthermore, the emission spectra were still analyzed with a narrow wavelength band, which does not allow the analysis or classification of initially unknown particles.

In Paper 3, the LEQ and the optical design were revised. During the research conducted for Paper 2, it was observed that the LIBS laser pulse causes a strong shockwave into the focusing chamber, which disturbs the focusing of the particles queued to reach the focus spot. Thus, the size of the LEQ was downscaled by reducing the rod diameters into 1 mm and the distance between adjacent rods into 7 mm (center-to-center). As estimated by Equation (13), this leads into more efficient
particle focusing and thus shorter waiting times for the focusing to stabilize after a laser pulse. The optical system was revised by utilizing non-planar arrangement of the optical elements and fiber optics, as illustrated in Figures 13 and 14. The revised design allows for more efficient monitoring of the particle focusing with respect to the LIBS laser. Furthermore, the revised emission optics collection design enables larger throughput of the emitted light and thus the use of a broadband multi-channel USB-spectrometer with a suitable resolution for simultaneous detection of multiple elements.

Figure 13. The optical setup of Paper 3. The particles were focused with a LEQ and triggered with the use of a 405 nm CW laser. The optical elements were divided into separate angles rather than one plane, leading to increased optical access to the focus spot. Adapted from Paper 3.

Figure 14 illustrates the emission collection system. As one of the main objectives was to enable wideband operation, the collection utilized a concave mirror in collimating the emission and a triplet lens in focusing it to minimize chromatic aberration. Light throughput was maximized with a custom-made fiber bundle with fibers arranged along the slits of the spectrometers, as shown in Figure 14. The
plasma forms mainly towards the opposite direction of laser propagation, starting from the focus spot (Thakur and Singh 2007). Thus, as the emission is collected perpendicularly with respect to the pulse laser, the noise caused by the plasma irradiation is minimized by focusing the emission collection strictly on the particle, rather than on the plasma formed in air. This enables to use short delay times after the LIBS pulse, which increases the signal from the analyte particle, as discussed in Section 4.2.

![Diagram of emission collection system](image)

**Figure 14.** The emission collection system of Paper 3 in more detail. The emission is collected utilizing a concave mirror and a triplet lens to minimize achromatic aberrations. Furthermore, the background noise by the plasma is minimized by collecting the emission from the side and focusing the collection directly on the particle, which is focused on the very edge of the plasma. Adapted from Paper 3.

A field-deployable platform (Spectroscopy Platform for Ambient Aerosol analysis, SPAA) was built based on the setup presented in Figures 13, 14 and Paper 3. The SPAA is presented in Figure 15. It is the first field-deployable device able to measure the composition of ambient particles with LIBS sampled from relevant concentrations of ambient air with the ability for high-resolution simultaneous multi-element analysis. It represents a significant advancement in aerosol measurement technology, as it offers a portable and affordable solution for analyzing particle composition in real-world applications on a single-particle level.

The SPAA was built on an optical breadboard mounted into a rack case to ensure eye-safe operation. The LIBS pulse is generated with a 355 nm Nd:YAG laser (Litron Nano SG 150-10, Litron Lasers Ltd.) and the emission signal is acquired with a 3-channel USB-spectrometer (AvaSpec-ULS4096CL-EVO, Avantes B.V.).
accessories required for the triggering system, particle charging, particle focusing, and spectrum acquisition are assembled into an aluminum rack on top of the rack case. The measurement is monitored and controlled by LabView software running on the measurement laptop. The dimensions of the SPAA are marked on Figure 15 and its mass is ca. 80 kg.

![Figure 15. The Spectroscopy Platform for Ambient Aerosol analysis (SPAA). A field-deployable platform was built based on the optical setup presented in Paper 3. The optical system is enclosed into a rack case to ensure eye-safe operation and the required accessory components are mounted into an aluminum profile rack on top of the case. The dimensions and main components are specified in the figure. Adapted from Paper 3.](image)

In the next chapter, the performance and limitations of the LIBS analysis conducted by the methods presented in Papers 1-3 are displayed, with the focus on the performance of the SPAA. Furthermore, optimization of measurement parameters is briefly discussed.
This chapter presents performance evaluation and limitations of the developed aerosol-LIBS systems. In Papers 1 and 2, the single particle spectra were acquired utilizing a table-top spectrometer and an ICCD camera with a narrow wavelength band. Thus, the composition of the measured particles was initially known, and the measurements were performed on a proof-of-concept level. In Paper 3, a broadband spectrometer was employed, and the multi-element capability was verified with more varying aerosol compositions, including an ambient aerosol sample. As the previous chapter focused on the results of Papers 1 and 2, this chapter focuses mainly on the results presented in Paper 3. The first section summarizes the LIBS measurement results of Papers 1 and 2, which lead the way towards the multi-element ambient particle analysis. In Section 4.2, the spectral processing routine of Paper 3 is presented along with results and discussion on emission signal optimization. In the last two sections, performance evaluation and particle classification results are presented from generated and ambiently sampled particles.

4.1 Towards relevant ambient particle analysis

The main results of Paper 1 are presented in Chapter 3, including the ability to trap particles for LIBS analysis into an EDB from the ambient air. With such ability, a clear advantage of ambient operation was confirmed with a comparison measurement to particles generated from droplets, presented in Figure 16. The figure includes LIBS measurements from wet-generated and dry-generated single kaolinite particles. It can be readily seen that the emission of calcium is dominant in the wet-generated case, but it diminishes to almost zero for the dry-generated particle trapped directly from aerosol phase. As presented in Paper 1, the wet-generated particles were generated using de-ionized water and namely clean equipment. Thus, requirement for water cleanliness in single particle composition analysis utilizing wet
generation is stringent, and the ability to avoid it by ambient sampling is highly beneficial.

![Figure 16](image)

**Figure 16.** Comparison between the spectra measured from kaolinite particles with dry- and water-based generation methods. The calcium peaks can be seen to diminish when trapping the particles directly from the aerosol phase. Modified from Paper 1.

With the EDB, the main issue considering ambient particle analysis was the slow analysis rate with a maximum of 1 analyzed particle per minute. Thus, the LEQ was employed to increase the rate. Furthermore, automatization of the LIBS analysis was developed to further increase the sampling rate and to enable autonomous measurements. In addition, the development of the Size-Amplification aided Aerosol Charger (SAAC) enabled to efficiently focus particles on the sub-micrometer range. An order of magnitude increase in analysis rate was obtained with the LEQ compared to the EDB, as shown in Figure 17, which shows the analysis rate and the hit ratio for 300 nm NaCl particles as a function of particle concentration. For the measurements, the aerosol was generated with a bubble generator and size-selected with a DMA (3081A, TSI Inc.) equipped with an impactor to remove doubly charged particles. The concentration was monitored with a condensation particle counter (CPC, 3776, TSI Inc.). A more detailed description of the measurement setup is presented in Paper 2. The optimal analysis rate was realized for particle concentrations in the order of 1 particle/cm³ and it was approximately 10 particles per minute. Smaller concentrations limit the analysis rate due to less overall particles reaching the analysis region and higher concentrations cause interference to the electrodynamic focusing due to electric forces between the particles, leading to false triggers and reduced hit ratio. The hit ratio, i.e., successful spectra divided by the amount of laser pulses, is in the order of 90 % for the small concentrations but declines after the concentration rises above the optimal concentration, due to the interference between the particles.
Figure 17. Hit ratio and analysis rate as a function of aerosol concentration for 300 nm NaCl particles, as presented in Paper 2. The optimal concentration can be seen to be at about 1 particle/cm$^3$, after which the hit ratio decreases due to interference between the particles in the LEQ. Adapted from Paper 2.

The advancements considering particle charging, focusing efficiency and analysis rate made during the research of Papers 1 and 2 were essential in the way towards the field-deployable platform presented in Section 3.3. In the following sections the performance of the platform and particle classification results are presented, preceded by a brief description of spectral data processing and signal optimization.

### 4.2 Spectral processing and signal optimization

This section presents the methods for spectral processing and signal optimization conducted with the Spectroscopy Platform for Ambient Aerosol analysis (SPAA). As each particle produces a single unique emission spectrum, they must not be averaged but instead processed individually. A background measurement without particles present was averaged from ca. 30 laser shots and subtracted from each particle spectrum. A peak finding algorithm was used to find the peaks in each spectrum and gaussian fits were utilized to define the exact peak position and area (functions `findpeaks` and `fit`, MATLAB 2020b, The MathWorks Inc.). The most prominent peak with least interference from adjacent peaks was selected as a marker for each recognized element. The detected elements and their corresponding peak wavelengths are presented in Table 1. A more detailed description of the signal processing method is provided in Paper 3.
Table 1. The observed elements during LIBS measurements of generated and ambient particles and the wavelengths (in nm) of the corresponding emission lines used in spectral analysis.

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelength</th>
<th>Element</th>
<th>Wavelength</th>
<th>Element</th>
<th>Wavelength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>396.2</td>
<td>Cu</td>
<td>213.6</td>
<td>Na</td>
<td>589.0</td>
</tr>
<tr>
<td>B</td>
<td>206.6</td>
<td>Fe</td>
<td>259.9</td>
<td>Si</td>
<td>251.6</td>
</tr>
<tr>
<td>C</td>
<td>229.7</td>
<td>K</td>
<td>766.5</td>
<td>Ti</td>
<td>335.0</td>
</tr>
<tr>
<td>Ca</td>
<td>393.3</td>
<td>Mg</td>
<td>279.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The emission signal was optimized in terms of laser pulse energy, gate delay and particle focusing with respect to the pulse laser. It was readily noticed that the optimum gate delay should be set to as short as possible. With traditional LIBS analysis, small gate delays lead to a strong background noise emitted by the plasma (Borduchi et al., 2022; Rai and Thakur, 2007). In our design, the emission collection optics presented in Figure 14 minimizes the collection of plasma irradiation, causing minimal plasma-induced interference to the analysis. Thus, the emission of the analyte particle can be recorded with a low delay without compromising the signal with a dominant background emission. Furthermore, different elements and their ionic and neutral emission lines have varying optimal emission time windows in LIBS analysis (Rai and Thakur, 2007). A low gate delay in a low-noise setting combined with a long gate width enables to include the optimal emission window of multiple emission lines into the same emission collection window with the spectrometer. Thus, gate delay of 100 ns and a gate width of 10 µs were used in the measurements conducted with the SPAA. Considering particle focusing, the same observation was made as presented by Järvinen and Toivonen (2016), i.e., the direct focusing of pulse laser to the particle leads to best signal from the analyte, originating from direct laser-particle interaction.

The effect of laser energy was studied more thoroughly, as its effect was immediately not so evident. For the optimization, two different aerosols were generated and size-segregated via a DMA (DMA 3081A, TSI Inc.). The samples consisted of 1.25 µm kaolinite particles and 1.0 µm salt particles including sodium chloride, magnesium sulphate and potassium chloride. The kaolinite particles were generated with a brush generator (RGB-1000, Palas GmbH) and the salt particles with custom-made bubble generator. A more detailed description of the aerosol generation system is available in Paper 3. The observed elements from the particles were silicon and aluminum (kaolinite), and magnesium, sodium and potassium (salt). The results of the optimization are presented in Figure 18.
Figure 18. Optimization of the LIBS pulse energy. In (a), the peak area for several elements were measured as a function of the pulse energy. Each marker presents the median of ca. 200 laser shots. The optimum for most elements were approximately 4-5 mJ, apart from Mg, which peaked at a slightly larger energy. In (b), the relative variance between single shots is presented as a function of laser energy, defined as the IQR of the single shots divided by the median peak area. Adapted from Paper 3.

In Figure 18 (a), peak areas of the elements are shown as a function of laser pulse energy. Each marker represents a median of ca. 200 analyzed particles. For most elements analyzed in the optimization series, the optimal laser energy is in the range of 4-5 mJ, except for magnesium, which peaks at a slightly larger energy. Moreover, it is readily observed that the emission line of magnesium exhibits the strongest peak area compared to the others, even with the lowest absolute mass within the particles, as described in Paper 3 and Figure 19 (a). The emission lines of other elements are closer to each other in intensity, but a clear difference can still be seen between sodium and potassium compared to silicon and aluminum, even with the kaolinite particles being larger in diameter and including a higher concentration of the analyte elements. This is because of the differences in the electron structures of the elements, as described in Section 2.1. Figure 18 (b) includes optimization results of shot-to-shot variation of the peak area as a function of laser energy. The variation is calculated by dividing the median peak area values shown in panel (a) by the inter-quartile range (IQR) of the ca. 200 peak area measurements. This leads to a quantity that describes the relative variation between subsequent spectra originating from similar particles. As can be seen from the figure, the variation is minimized with about 5 mJ of laser pulse energy. In the light of the optimization, a laser energy of 4.5 mJ was used in further measurements.
4.3 Composition measurements and particle classification

The analytical performance of the SPAA was evaluated with a mixture of test particles with well-defined composition. Four different salt solutions with MgSO₄, NaCl and KCl were prepared with known compositions and generated with a custom-made bubble aerosol generator. These salt solutions were chosen as their emission lines are widely separate, with prominent peaks at 279.6 nm, 589.0 nm and 766.5 for Mg, Na and K, respectively. Thus, the emission spectra were acquired utilizing all the spectrometers of the 3-channel USB-spectrometer. The particles were size segregated with a DMA (DMA 3081A, TSI Inc.) to yield nearly monodisperse size distributions of 0.8, 1.0, 1.25 and 1.5 µm diameter particles. The particle size distribution and concentration were monitored utilizing an Aerodynamic Particle Sizer (APS 3321, TSI Inc.). As the generated size distribution of the particles after the bubble generator had significantly smaller median size than the classification size selected with the DMA, only a small amount of multiply charged particles were sampled from the generation system. With four different compositions and four different particle sizes, the sample particles consisted of a total of 16 different absolute masses for each element. The results of the performance characterization are presented in Figure 19.

Figure 19 (a) includes the measured peak areas as a function of initially known masses per element in a particle. Each marker is the median value of at least 200 single particle measurements. One composition sample of 1.0 µm particles was used as a reference for a linear calibration of peak area per mass of element. With the calibration, the peak areas presented in (a) were transformed into masses from LIBS measurements and plotted as a function of the actual mass. The ‘measured’ versus ‘actual’ mass results are presented in Figure 19 (b). In (a) and (b), the error bars are the IQR of the measured peak area and of the mass. The horizontal IQR originates from the fact that the size distribution generated by the DMA is not strictly monodisperse but has a geometric standard deviation of about 1.2, as measured by the APS. As can be seen from Figure 19 (b), the error bars are almost identical with respect to mass, thus most of the variance in measured mass is most likely due to the variance in particle size.
Figure 19. Results from the performance analysis of the SPAA. Mg, Na and K were simultaneously detected from generated salt particles with different well-defined compositions. In (a), the peak areas of emission lines are presented as a function of element mass in a particle. A calibration sample is presented by black markers and used in (b) to evaluate the resolution power in terms of absolute mass of an element per particle. In (c) and (d), the same calibration sample is used to evaluate the resolution power in terms of relative mass fractions between the three elements. A comparison to XRF is also conducted in the latter two figure panels. The different elements are denoted with different colors and the XRF sample is denoted with the asterisk signs. The error bars in (a) and (b) are the IQR of the peak area and of the mass of an element, calculated from the spectral data and the measured particle size distribution data. Adapted from Paper 3.

Considering relative fraction of the analyte elements in a particle, the same calibration sample was used to compare the measured fraction to the actual one. Figure 19 (c) and (d) include these results with a comparison to X-Ray Fluorescence (XRF) measurement from a bulk sample of the same salt composition. As can be
seen, the LIBS measurement overcome the XRF measurement performance for each sample composition. In (d), the measured fraction has been divided by the actual fraction and the LIBS measurements have been marked with horizontal lines for readability. Most of the LIBS measurements stay within 25% of the actual value. For magnesium, the smallest particle size of 0.8 µm, marked as crosses, has the most deviation in the fraction, most likely due to the absolute mass being close to the limit of detection (LOD). The LOD values were estimated as the values producing a detectable signal for over 75% of the laser shots. The values in absolute mass were found to be approximately 2, 40 and 70 fg for Mg, Na and K, respectively. These correspond to particle sizes in the range of ca. 100-400 nm in diameter with pure salts of MgCl, NaCl and KCl.

Overall, the method showed excellent quantitative performance with a simple single-point calibration, spanning over multiple orders of magnitude in absolute and relative mass. The optimal analysis rate was found to be approximately 20 particles/minute, showing a modest 2-fold increase to the previous LEQ design. The ability to resolve elementary masses in individual particles in the femtogram range with a wideband spectrometer without an intensified detector is unprecedented.

In addition to the salt aerosol analysis, Arizona test dust (ATD), kaolinite and ISO test dust were generated with a brush aerosol generator (RGB-1000, Palas GmbH) and analyzed with the SPAA. Figure 21 includes example single particle spectra from each of the generated particles (a) – (d), including the average spectra of 30 background shots (e). As discussed in Sections 2.1 and 4.2, different elements exhibit different emission intensities with the same number of atoms present in the sample, due to variations in their electron structure. With certain boundary conditions, the expected proportions of the emission intensities can be estimated utilizing statistical methods, given that the electron temperature and density are defined. Using emission peaks of singly ionized calcium from ATD and ambient particle measurements, the Boltzmann plot method presented in Section 2.1 was utilized to define the median apparent temperature of the plasma (Bousquet et al., 2023), found to be 1.0 eV/k_B (11600 K). This temperature was used with an electron density of \(10^{17}\) cm\(^{-3}\) to acquire reference spectral data from NIST LIBS database for each analyzed element (Ralchenko and Kramida, 2020). A single example Boltzmann plot constructed from the peaks of Ca of an ambient particle is shown in Figure 20.
Figure 20. An example Boltzmann plot constructed from the emission peaks of singly ionized calcium measured from an ambient particle. The slope of the linear fit is defined in Equations (3) and (4) as $-\frac{1}{\kappa B T}$ and can thus be used to determine the plasma temperature. For this single measurement, the temperature is found to be 1.1 eV/$k_B$.

The spectral analysis presented in Section 4.2 was conducted for each reference spectrum, and the peak areas acquired from the analysis were utilized as element-dependent normalization factors. Spectrometer-dependent factors acquired from the performance analysis measurements presented in Figure 19 were combined to the ones obtained from the reference data analysis. These factors were used together to normalize the acquired peak areas into proportional number of analyte elements present in the particles on a single particle basis. Some of the measured n-% shares of the measured elements in the generated particles are presented in Figure 22.

Nitrogen and oxygen are present in the ambient air, as can be seen from the background spectrum in Figure 21 (e). Moreover, their peaks are still present in the particle spectra shown in Figure 21 (a) – (d), even with the background subtraction. This is most likely due to the different spatial distribution of the plasma when it is initiated by the laser-particle interaction. For oxygen-containing particles like kaolinite, no change in the proportions of oxygen and nitrogen emission intensities was detected compared to other particle types. Thus, N and O were assumed to mainly originate from the surrounding gas rather than the particles and were not used in the proportional normalization of elements present in the particles.
Figure 21. Example single particle spectra measured from generated aerosols and the background average spectrum from 30 LIBS pulses. In spectral analysis, the background is subtracted from the single particle spectra. The spectral area between the dashed lines in (a) – (d) is recorded but includes no relevant data considering the particles presented here. Modified from Paper 3.
Figure 22. Approximate proportional number concentrations of the elements measured from test aerosols. The colors represent different elements, and each bar stack represents one particle. The normalization has been conducted by utilizing NIST LIBS database and the measured line intensities for the elements. Adapted from Paper 3.

Figure 22 shows the proportional number concentrations of the elements present in the test aerosol particles. ATD contains the most complex external and internal mixture of different elements, kaolinite is mainly consisted of aluminum and silica, and the ISO test dust is mainly silica. The results are in good agreement with literature values (Vlasenko et al., 2005; Hu and X. Liu 2003). In the next section, results from an ambient aerosol sample are presented with the same normalization routine conducted for the particles.

4.4 Ambient particle classification

Ambient aerosol was sampled through the laboratory window during a 40-minute sampling period on 2.8.2023 afternoon. A total of 313 particle spectra were detected, consisting of particles of 1-3 µm in diameter. A more detailed description of the sampling setup is presented in Paper 3. With the aid of multi-element analysis and the normalization routine presented in Section 4.3., the particles were divided into distinct categories based on their elementary composition. The distinguished categories were “Salt”, “Biological”, “Dust” and “Carbonaceous” particles. The abundance and strict criteria of classification to the categories are shown in labels of the sections of Figure 25. Figure 23 includes typical examples of single particle
spectra from each category, and Figure 24 includes ten first spectra from each category. From Figure 24 it can be noticed that the categories have easily recognizable spectral footprints. However, the “Biological” and “Carbonaceous” particles seem to be nearly identical. The difference is more easily observed from Figure 23, which includes the raw spectral data of the particles.

![Spectra from each category](image)

**Figure 23.** Example single particle spectra from the ambient aerosol sample. The spectra represent the 4 main categories distinguished during the measurement. Broadband operation of the SPAA enables to resolve multiple elements from each particle simultaneously, enabling particle classification. Modified from Paper 3.

When comparing the spectral data of the groups, it is evident that the “Biological” group includes strong signal of Ca and/or K, but the “Carbonaceous” only includes C. The difference is almost entirely lost in the n-% normalization, the emission line intensity of C is more than an order of magnitude weaker than the one of K and Ca.
Thus, the normalization described in Section 4.3. corrects the “Biological” particles to mainly consist of C. It should be noted that the normalization is only conducted between the elements that were detectable during the measurements. Thus, for example water (i.e. H and O) is not included in the normalization.

![Example spectra from the categories of the ambient aerosol sample. The n-% values are acquired utilizing the method described in Section 4.3. and Paper 3. The colors represent different elements, and each bar stack represents one particle. Adapted from Paper 3.](image)

Figure 24. Example spectra from the categories of the ambient aerosol sample. The n-% values are acquired utilizing the method described in Section 4.3. and Paper 3. The colors represent different elements, and each bar stack represents one particle. Adapted from Paper 3.

The abundance of each category during the measurement period is presented in Figure 25. The most abundant category was “Salt” particles with a 28 % share of the spectra. “Biological”, “Dust”, and “Carbonaceous” categories were 20 %, 20 % and 7 %, respectively, 11 % were unclassified and 13 % were misses. The unclassified particles consisted mainly of Na- and Ca- rich particles that could not be classified in any of the main categories. The misses could have been actual misses or included only non-detectable elements.
This is the first time that LIBS has been employed for ambient particle measurements with a multi-element capability. The categories are based on prior knowledge on aerosol composition of different particle types (e.g. Seinfeld and Pandis 2016, p. 354; Saari et al., 2016; Usher et al., 2003; Heldal et al., 1985) but the measurement includes no comparison with other measurement techniques. Thus, the division is an estimate of the local aerosol population but may include bias due to the sampling strategy and the category division could be further discussed. The trajectory of the local airmass was determined utilizing the HYSPLIT data from NOAA archive and found to have travelled above the Baltic Sea prior to arriving to the sampling site (Stein et al., 2015). This could explain the strong “Salt” particle abundancy. The “Dust” category is easily recognized due to strong abundance of Silica and Aluminum in the particles. The “Biological” particles are probably the most uncertain category, as combustion related particles are also often rich in carbon. However, the presence of K and Ca combined with the lack of other metallic compounds suggest that the measured particles are of biological origin, rather than combustion related (Jahn et al., 2021; Yatkin and Bayram 2007; S.S. Park and Kim, 2005).
The goal of this thesis was to develop technology capable of analyzing the composition of ambiently sampled single particles utilizing laser-induced breakdown spectroscopy (LIBS) in a real-world setting. Major breakthroughs were presented considering more efficient particle charging, particle trapping and focusing from initially uncharged aerosol, and the multi-element LIBS analysis of initially unknown aerosol, sampled directly from the ambient air.

Our basic assumption for the most efficient use of LIBS in aerosol analysis was that individual particles must be precisely focused into the same focal volume with the pulse laser utilized in LIBS. Thus, the first 2 papers mainly focused on the methodology to achieve this for initially uncharged aerosols. In Paper 1, a high-field corona charger was presented and characterized. Most of the prior research including aerosol focusing with the electrodynamic balance (EDB) is focused on aerosols generated by droplet generation where particles easily achieve the Rayleigh limit. Thus, the stability of an electrodynamic balance (EDB) trap was studied for particles with a low charging state utilizing numerical methods such as electric field and particle trajectory simulations, presented in detail in the supplementary information of Paper 1. The results of the charger characterization and the EDB stability studies were combined with experimental measurements. Ultimately, ambiently sampled supermicron particles could be analyzed with an EDB-LIBS system with the use of the new aerosol charger.

With the results from Paper 1 at hand, it became evident that initially uncharged particles below a few micrometers in diameter will not acquire enough charge for efficient focusing with utilizing only a corona charger. Thus, the Size-Amplification Aided Aerosol charger (SAAC) was developed and presented in Paper 2. The SAAC utilizes condensation growth of particles prior to charging to enable efficient field charging effect. As the particles are dried after the charging, they end up with a high electrical mobility, increasing as the particle size reduces. This was found to lead into efficient particle focusing in an EDB for initially neutral aerosol particles with an arbitrary particle size. Sampling ambient particles into an EDB without size limitations has not been possible with prior charging methods, highlighting the significance of the SAAC system. Furthermore, in Paper 2, a linear electrodynamic
quadrupole (LEQ) was employed to increase the sampling rate. In the LEQ the focusing is conducted in only 2 dimensions leading to a flow-through system. Further particle trajectory and electric field simulations were conducted to yield a relaxation time, which can be used to estimate the time it takes for a particle to reach the focal line from an initial displacement in the focusing chamber. With an estimate of the relaxation time, dimensions of a LEQ or EDB and required particle charging systems can be effectively designed.

In Paper 3, the Spectroscopy Platform for Ambient Aerosol analysis (SPAA) was presented. With the platform, ambient aerosol particles can be analyzed from relevant number concentrations on a multi-element, single particle level. The platform is a breakthrough in aerosol composition analysis, providing an alternative method for single-particle mass spectrometry. As presented in Sections 4.3-4.4., SPAA showed excellent quantitative performance in absolute and proportional mass analysis for the tested salt compositions on a single particle level, exceeding the resolution of bulk sample XRF. Furthermore, the multi-element capability enabled to divide the ambient aerosol particles into distinct categories based on their elemental composition. It is noteworthy to point out that the analysis was conducted with the aid of a three-channel USB-spectrometer equipped with non-intensified detectors. Thus, even with the reported ten-fold decrease in sensitivity compared to a more expensive intensified sensor, particles could be analyzed and classified in a real-world setting (Carranza et al., 2003).

Overall, the main research objective, to develop an instrument capable of measuring the composition of ambiently sampled individual aerosol particles with LIBS, was successful. During the research, aerosol charging methods towards a higher charging state were developed and characterized. Furthermore, the focusing efficiency of an EDB or LEQ was researched, and practical equations were developed to aid in the design of such systems. The developed optical design enables to maximize the acquired emission signal from small masses of elements down to particles below 1 micrometer in diameter. The minimum detectable particle size is in the order of 200 – 800 nm, depending on the particle composition and on the attainable triggering signal.

Future research options with the method are vast. Considering methodology development, the sampling rate could still be increased with more consideration given to the aerosol flow system. With the combination of the LEQ and efficient aerodynamic focusing, the flow rate through the system could be highly increased leading to analysis rates potentially above 1 particle per second. Furthermore, by minimizing the electrical losses of the SAAC, higher sampling rates could be reached
for even smaller concentrations. Another direction of instrument development would be employing an echelle spectrometer with an intensified detector for emission analysis. As discussed earlier, that might lead into an order of magnitude increase in sensitivity, thus enabling sub-femtogram absolute mass determination for highly luminous elements like magnesium or calcium. More importantly, increased dynamic sensitivity might enable to resolve elements that were not seen during the measurements conducted with the USB-spectrometer, such as sulfur or hydrogen. Adding more spectroscopy methods, like Raman and laser-induced fluorescence spectroscopies to the analysis would increase analytical power and provide insight of the biological and molecular properties of single particles.

Future research should also include extensive utilization of the field-deployability of the SPAA to provide datasets from various sources and locations. Potential study areas include ice-nucleation studies, in which the SPAA could be taken into either a cloud environment or combined with an atmospheric simulation chamber to provide direct information about ice nuclei residual particles (Cornwell et al., 2019; Pratt et al., 2009). Another field of study could be non-combustion related traffic emissions, which are often rich in metals and prevalent in the coarse aerosol (d_p > 1 µm) mode in size (Piscitello et al., 2021). A third example application would be pathogen aerosol detection and monitoring, as the high sensitivity combined with a broad spectral range enables for more accurate elemental analysis and thus more potential classification power (Saari et al., 2016; Hybl et al., 2006).
6 REFERENCES


PAPERS
Paper 1

Toward elemental analysis of ambient single particles using electrodynamic balance and laser-induced breakdown spectroscopy.


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Toward elemental analysis of ambient single particles using electrodynamic balance and laser-induced breakdown spectroscopy

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ABSTRACT
In this article, we present a novel method for the elemental analysis of airborne aerosol particles using electrodynamic balance (EDB) trapping followed by laser-induced breakdown spectroscopy. The setup consists of a newly designed corona-based aerosol charger, double-ring electrodynamic balance trap and optical arrangement for the spectroscopy. Experimental laboratory measurements using the method show that the minimum particle size for successful analysis is 1 μm in diameter, and the minimum airborne concentration is of the order of 1 particle/cm³. In addition to the method, we will present results on the charging efficiency of the developed charger and novel stability analysis of the EDB at the charge region. The results from the stability analysis will ease the way toward analyzing submicron particles with the technique.

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1. Introduction
Particulate matter (PM) affects human wellbeing both directly through breathing and indirectly by taking part in atmospheric processes, such as the hydrological cycle and radiation balance: PM smaller than 10 μm in diameter can penetrate through the nasal passages of the respiratory tract and cause adverse health effects (Kim, Kabir, and Kabir 2015). PM also takes part in cloud formation and droplet freezing, thus affecting precipitation processes and albedo (Carlson et al. 2001; DeMott et al. 2010; Murray et al. 2012). Moreover, lack of knowledge about PM driven droplet freezing dynamics in clouds is one of the main obstacles in a way of better understanding and predicting the climate system (DeMott et al. 2010; Vergara-Temprado et al. 2018).

Determining elemental composition provides crucial information about the aerosol species, sources and toxicity potential (Calvo et al. 2013; Schleicher et al. 2011). Thus, several studies have concluded the importance of elemental characterization of PM (e.g., Hoosse and Möhler 2012; Kim, Kabir, and Kabir 2015; Knopf, Alpert, and Wang 2018; Paramonov et al. 2019). An extensive range of analysis methods have been established for particles collected on filters or impactors, capable of analyzing a broad variety of chemical properties up to the spatial distribution of molecular composition (see, e.g., Fletcher et al. 2011; Laskin et al. 2003). However, long sampling times in offline analysis restricts the observation of temporal variation of ambient aerosols. Also, contamination and evaporation and/or condensation of vapors may cause measurement artifacts to the analysis and single-particle resolution may be lost (Maeng et al. 2017; Turpin, Huntzicker, and Hering 1994).

Online analysis methods overcome many of the problems considering offline analysis, as direct analysis from ambient air enables to preserve temporal variability, volatile particle compounds and single-particle resolution. To date, the most common real-time technique to analyze chemical composition of ambient PM is aerosol mass spectrometry (Nash, Baer, and Johnston 2006). Though accurate and sensitive, mass spectrometry has certain shortcomings: the equipment is complicated and expensive, requires a good vacuum and relatively heavy data.
analysis to interpret the measurement results. Another possible technique for the online elemental analysis of (particulate) matter is laser-induced breakdown spectroscopy (LIBS) (Laserna, Vadillo, and Purohit 2018). It has the ability to classify every element in the periodic table without complicated sample preparation or a vacuum. Thus, LIBS is a widely used technique in different fields of research (e.g., Hamzaoui et al. 2011; Rai and Rai 2008; Vaniman et al. 2014), including aerosol science (Essien, Radziemski, and Sneddon 1988; Kim et al. 2019; Xiong et al. 2016).

In LIBS, a laser pulse is focused into a small volume of the order of 10–100 μm³ (Järvinen and Toivonen 2016). The signal originates only from this volume and thus the analyzed material must be within that volume. In order to obtain LIBS signal from PM, the particles can be collected on a substrate such as a filter (Panne et al. 2016) or an electric needle tip (Diwakar, Kulkarni, and Birch 2012). Without particle collection, a reasonable statistical probability of the laser hitting a particle can be achieved with large local particle concentration combined with a high pulse rate (e.g., Gallou et al. 2011; Hahn and Lunden 2000). In order to improve the statistical probability, the aerosol can be focused into a narrow stream with a nozzle and sheath flow (Park, Cho, and Kwak 2009; Tjärnhage et al. 2013). Fast sampling rates have been achieved for reasonable concentrations (> 1000 particles/cm³) of ambient PM by Maeng et al. (2017), by combining timed ablation (as in Manninen et al. 2008; Tjärnhage et al. 2013) with aerosol flow focusing.

LIBS analysis of spatially focused single particles have been reported using methods including droplet generation and trapping (Contreras et al. 2018; S. T. Järvinen et al. 2014) and optical resuspension from a substrate combined with optical trapping (Fortes, Fernández-Bravo, and Laserna 2014). Water droplets have been focused with a standing acoustic wave (Contreras et al. 2018) and with an electrodynamic balance (EDB) trap (Järvinen et al. 2014). Furthermore, primary particles can be immersed in the water droplets and the dry residuals analyzed with the EDB-LIBS equipment, leading to a single-particle analysis technique (Saari et al. 2016). However, droplet generation leaves the residual particles with unwanted contamination from the carrier substance.

Using EDB focusing, Vehring et al. (1998) successfully analyzed highly charged droplet residual particles originating from a vibrating orifice generator source (VOAG; Berglund and Liu 1973) with Raman spectroscopy, down to a minimum diameter of 3 μm. For ambient particles, Raman spectroscopy revealed challenging because of photophoresis overtaking the electrical focusing force in the EDB. However, a few large (dₚ > 10 μm) particles were analyzed.

In this article, we present an EDB–LIBS technique for the direct analysis of airborne single particles. To our knowledge, no prior trapping techniques have been combined with LIBS directly for ambient aerosol sources before. In LIBS, photophoresis is not seen as a problem, since the pulse times are short and the emission spectrum is collected in the order of milliseconds. The focus on the presented results will be on the trapping stability of the EDB, since it emerged as the most limiting factor of the technique. This is due to the achieved relatively low particle charge compared to previously used droplet charging methods. Consequently, we present new methods to evaluate the trapping efficiency. The EDB-LIBS technique shows potential for single particle chemical analysis applicable for instance to composition analysis of ice residual particles or monitoring ambient particles with potential adverse health effects.

2. Materials and methods

The strength of the electric interaction between the particles and the focusing electric field sets the biggest challenge for the spatial focusing in the EDB. Since particle focusing is essential for the LIBS analysis and dependent on the particle charge, an aerosol charger was designed to maximize the charging state of large (dₚ > 0.5 μm) particles. The charge distribution produced by the charger was measured and the results were applied for the analysis of the EDB focusing stability. Laboratory measurements with the EDB-LIBS method were then conducted with two different aerosol generation methods using kaolinite mineral particles.

2.1. Charger design

Operation of a corona discharge-based aerosol charger relies on two major phenomena: charging due to ion diffusion and charging due to electric field in the charging region. Ion diffusion is considered the dominant charging process for small (dₚ < 200 nm) particles and field charging for large particles (e.g., Hinds 1999). The phenomena will not be discussed in detail here, but for spherical particles the charging efficiencies due to them can be estimated by equations

\[ n_d = \frac{2\pi e\sigma d_p kT}{e^2} \ln \left( 1 + \frac{d_p e^2 N_i t}{8 e_0 kT} \right) \quad (1) \]

and

\[ n_f = \left( \frac{3e}{\epsilon + 2} \right) \left( \frac{E \pi e \sigma d_p^2}{e} \right) \left( \frac{\pi e Z_i N_i t}{4 \pi e_0 + \pi e Z_i N_i t} \right), \quad (2) \]
where $n_d$ and $n_f$ are the charging efficiencies of a diffusion and a field charger, respectively (Hinds 1999). Terms in the diffusion charging Equation (1) are the permittivity of the vacuum $\varepsilon_0$, particle diameter $d_p$, the Boltzmann constant $k$, absolute temperature $T$, mean thermal velocity of the ions $c_i$, the elementary charge $e$, ion concentration in the charging zone $N_i$ and the residence time of the particle in the charging volume $t$. In Equation (2), the permittivity of the particle $\varepsilon$, the ion electrical mobility $Z_i$, and the electric field $E$ also add to the final charge of the particles.

Typical diffusion chargers provide below 100 elementary charges per particle at one micrometer of particle size (e.g., Liu and Pui 1977; Park, An, and Hwang 2007; Rostedt, Marjamäki, and Keskinen 2009). With field chargers, higher charge numbers for the particle size have been achieved (Hewitt 1957; Unger, Boulaud, and Borra 2004), with over 400 charges per particle in the Hewitt’s oscillating square field-type charger. The new charger presented in Figure 1 is designed in a way that the electric field in the charging region is enhanced by the same voltage that causes the corona discharge itself. The design obviates the need of an oscillating field, therefore simplifying the charger and the equipment requirements.

The corona discharge takes place at the end of a short wire ($d = 0.2$ mm), located at the tip of the inner tube. In the prototype the wire, made of stainless steel, is spot-welded into the middle part of the inner tube and brought toward the tip inside heat-shrink tubing. The length of the wire is 2 mm from the exit of the inner tube. Since the whole inner tube is at high potential, the field applied to particles inside it is small due to symmetry. Large atmospheric particles also typically have low electrical mobility (Fuchs 1963), leading to low electrical losses inside the tube. The electric field strength in the charging region was calculated using a finite element analysis software (COMSOL Multiphysics® 5.3.1, Comsol Inc.), and was found to be of the order $10^5$–$10^6$ Vm$^{-1}$, as seen from Figure 1. The charger is used with a 2 lpm flow rate and a constant voltage of 5.10 kV, which corresponds to an electric current of about 20 $\mu$A. The inner diameters of the inner and outer tubes are 2.0 mm and 13.0 mm, respectively.

### 2.2. Charger performance measurements

The charge distribution and the geometric and arithmetic mean values of the charging state were measured as a function of particle size. To generate a well-defined monodisperse aerosol at the size range of 0.5–5 $\mu$m, the single charged aerosol reference (SCAR) system (Yli-Ojanperä et al. 2010) was used. In SCAR, small (approx. 10 nm) silver particles are singly charged, classified with a nano-DMA and grown with diethylhexyl sebacate (DEHS). The DEHS particles are then classified into a monodisperse aerosol with a differential mobility analyzer (DMA) designed to classify especially large (up to 5.3 $\mu$m) particles (Tampere Long DMA, Järvinen, Keskinen, and Yli-Ojanperä 2018). The particles leaving the DMA are thus monodisperse and carrying a single negative elementary charge.

After the generation, the aerosol was charged with a positive charge using the presented charger and then analyzed using setups presented in Figure 2. As studied before (e.g., A. Järvinen et al. 2014; Qi et al. 2009), the small initial charge is not expected to affect the charger performance. The carrier gas in the charger efficiency measurements was dry air (RH < 10%, $T \approx 295$ K), with a slightly increased (80 – 82%) nitrogen concentration due to the silver particle generation. A particle counter (CPC II, model 3756, TSI, Shoreview, MN, USA) was placed after the charger in parallel to the alternative measurement setups as a reference to monitor concentration stability and to normalize the measurement points.

The charge distribution measurement setup is presented in the middle branch of Figure 2. The charged
aerosol was classified by another DMA (nano-DMA, model 3085, TSI Inc., Shoreview, MN, USA [Chen et al.1998]). After the nano-DMA, the aerosol enters a condensation particle counter (CPC I, model 3750, TSI), from which one can define the charge distribution density function shape using the particle concentration as a function of the nano-DMA voltage (for further information see the online supplementary information [SI], Chapter 1).

The arithmetic mean charge was measured using a Faraday cup electrometer (FCUP) and a CPC (CPC II), as shown in Figure 2. With the FCUP, a total electric current \( I \) carried by an aerosol can be measured (see, e.g., Dhaniyala et al. 2011). If the number concentration of particles \( N \) and flow rate \( Q \) through the FCUP are also known, one can calculate the arithmetic mean of elementary charges \( n \) per particle:

\[
n = \frac{I}{QNe}.
\]  

Identical transportation lines and flows into the CPC and the FCUP were used to minimize asymmetric particle losses and the concentration values were corrected by the detection efficiency of the particle counter. The right measurement branch in Figure 2 was used in the EDB stability characterization, presented in the next chapter.

2.3. Electrodynamic balance

After the charger, the particles are introduced into the EDB chamber. The functional part of the EDB is the double-ring electrode configuration presented by Heinisch et al. (2009). Several authors have studied the principles of the balance analytically (e.g., Davis 1985; Frickel, Shaffer, and Stamatoff 1978; Hartung and Avedisian 1992) in a sophisticated manner. The force equation considering a particle in an electric field is derived from Newton’s second law:

\[
F_s + F_g + F_E + F_{\text{ext}} = m \frac{d^2r}{dt^2}
\]  

in which the first term \( F_s \) is the Stokesian drag force, \( F_g \) gravity, \( F_E \) electrical force due to the electrical field and \( F_{\text{ext}} \) consists of possible external forces, caused by convective forces or radiation pressure, for example. When assuming that the particle stays in the Stokes regime while oscillating and that the external forces are negligible, expanding Equation (4) at the symmetry axis (noted as \( z \)-axis) leads to

\[
-\frac{3\pi \eta d_p}{C_c} \frac{dz}{dt} + qE_{\text{AC}}(z)\cos(\omega t) + qE_{\text{DC}}(z) - mg = m \frac{d^2z}{dt^2}.
\]  

In earlier work (e.g., Davis 2011), Equation (5) has been expressed using dimensionless variables \( Z = \frac{z}{z_0} \) and \( \tau = \frac{\omega t}{2} \), where \( z \) is the distance of the particle from the focus spot, \( 2z_0 \) is the distance between the DC electrodes (here \( z_0 = 4 \) mm) and \( \omega \) is the angular frequency of the AC-voltage. The equation thus simplifies into the dimensionless form:

\[
\frac{d^2Z}{d\tau^2} + \delta \frac{dZ}{d\tau} + 2\beta Z \cos(2\tau) = \sigma,
\]  

in which the drag parameter \( \delta \propto \frac{1}{d_p} \) and the AC-field strength parameter \( \beta \propto \frac{V_{\text{AC}}}{V_{\text{DC}}} \) define the stability and the DC offset parameter \( \sigma \propto \frac{V_{\text{DC}}}{V_{\text{DC}}} \frac{1}{\omega^2} \) defines the oscillation amplitude if the DC-voltage is not correctly set to balance external forces (Davis 2011). Other terms in Equations (5) and (6) are \( \eta \), which is the dynamic viscosity of the carrier gas, \( d_p \) is the diameter of the particle, \( m \) its mass, \( q \) its electric charge and \( C_c \) is the slip correction factor. \( V_{\text{AC}} \) and \( V_{\text{DC}} \) are the (amplitude) AC- and DC-voltages and \( V_{\text{DC}} \) is the DC-
voltage needed to balance the particle at the focus spot. In Equation (6), the DC-component of the electric field (DC-field) is defined as independent with respect to $z$. The assumption is reasonable in the case of highly charged droplets and droplet residuals, since they interact strongly with the AC-field and thus drift efficiently into the close proximity of the focus spot.

Setting the offset parameter to $\sigma = 0$ and solving Equation (6) as a function of the stability parameters, earlier studies have presented multiple instability regions similar to the ones solved and presented in Figure 3 (e.g., Davis 2011; Davis 1985; Frickel, Shaffer, and Stamatoff 1978; Hartung and Avedisian 1992). In these unstable regions, the AC-field causes a highly charged particle to oscillate violently and escape from the trap. Using measured values of particle charges achieved with the charger presented in the previous chapter should be well in the stable area of the chart with an amplitude AC-voltage of 1 kV and an AC-frequency of 100 Hz.

It can be seen from Figure 3 that the parameter values calculated for all of the particles under consideration fall into the stable region of the chart. However, experiments show that submicron particles charged with a corona-based charger neither stably trap into the focus spot nor oscillate violently, but instead slowly drift away from the trap. The phenomena was also noted by Aardahl et al. (1997), who studied the convective forces causing the instability.

In our study it was noticed that it is also the DC-field that leads to unsuccessful balancing: with a low charge the DC-field needs to be greater to cancel out the effect of gravity and on the other hand the interaction with the balancing AC-field becomes weaker. Thus, the spatial inhomogeneity of $E_{DC}$ can not be neglected from the stability consideration as was made in Equation (6).

The instability caused by the DC-field was studied both numerically and experimentally. Numerical methods include simulations of the electric field components in the EDB, which were then applied to particle trajectory simulations by solving the differential Equation (5) numerically (ode45 solver, Matlab R2017b, The MathWorks) with a multitude of different parameter values. Ultimately, an equation for the minimum amplitude of the AC-voltage required for successful trapping was derived from the trajectory simulations. The simulations are presented in more detail in the SI, Chapter 2.

As will be presented later in Section 3, the threshold AC-voltage equation was found to be a function of the particle electrical mobility and the initial position and of geometrical constants of the EDB. The equation was verified experimentally with multiple different combinations of particle electrical mobilities, diameters and initial positions. The measurement setup of the threshold voltage is presented in the right branch of Figure 2: a nano-DMA was used to classify the charged monodisperse DEHS aerosol as a function of its electrical mobility, independent of the particle size. The measurements were conducted by choosing a certain particle electrical mobility with the nano-DMA, trapping a particle with that mobility and manually finding the right DC-voltage needed to keep the particle in the focus spot. After that, the particle was deviated to a known, pre-defined distance from the focus by temporarily increasing the DC-voltage. Once the midpoint of the oscillation of the particle was on that distance, the DC-voltage was set back to the balance value and a threshold AC-voltage needed to drift the particle toward the focus spot could be defined. Measurements were made with multiple electrical mobilities, 4 different particle diameters (2, 3, 4, and 5 $\mu$m) and from 2 different initial particle positions (0.5 mm and 1.0 mm) with an AC-frequency of 100 Hz. A virtual impactor with a cut-point of approximately 1 $\mu$m was used as a flow splitter in front of the EDB, due to the flow difference between the EDB ($Q_{EDB} < 0.1$ lpm) and the charger ($Q = 2$ lpm).
2.4. EDB-LIBS analysis

The measurement principle is presented in Figure 4a: The aerosol under analysis is charged and then driven to the EDB chamber through a virtual impactor (VI). The VI operating at a major flow of 2 lpm ensures an approximately constant flow through the charger, since the flow rate through the EDB chamber is small ($Q_{\text{EDB}} < 0.1 \text{ lpm}$) or zero, depending on the phase of the analysis. It also minimizes the particle losses caused by the flow difference between the charger and the chamber, for particles larger than its cutpoint (approx. $d_{p} > 1 \mu m$).

The chamber itself, presented by Järvinen et al. (2014), includes optical windows located on every side of the chamber and in the top and bottom, allowing optical access through the middle electrodes. Schematic figure of the chamber is shown in Figure 4b. The trapping volume is illuminated from the bottom window with a 532 nm CW laser (CW532-005, Roithner Lasertechnik GmbH, Vienna, Austria). Outer electrodes are set on ground potential and the inner ones include both AC- and DC-components of the balancing voltage, as presented by Heinisch et al. (2009). The aerosol flow is introduced into the chamber with an inlet from one of the side windows and directed through the upper electrode, therefore through the trapping volume. When the aerosol is flowing through the chamber, the flow is stopped and, if successful, a particle is trapped in the electric field. If multiple particles are trapped, they can be driven outside by temporarily unbalancing the DC-voltage. Usually the DC-voltage needs to be adjusted separately for each particle to drive it to the exact focus spot. When the particle, monitored with a CMOS-camera (DCC1545M, Thorlabs, Inc., Newton, NJ, USA), is within the focal volume of the pulse laser, it is manually triggered and a plasma emission spectrum can be collected by the spectrometer connected to an ICCD-camera (DH340T-18U-E3, Andor Technology Plc., Belfast, UK).

Two experiments were conducted using the same aerosol source with different generation methods. The used test sample was kaolinite mineral dust (CAS Number 1318-74-7, Sigma-Aldrich Corp., St. Louis, MO, USA), which consists of aluminum, silicon, oxygen and hydrogen. The first generation method was a wet generation method using a piezo-electric droplet dispenser as in Järvinen et al. (2014). The second method was a dry generation method using a simple glass vial attached to a magnetic stirrer, which produced a polydisperse aerosol in the size range of 1–10 μm. When using the powder generation method, the aerosol was first pre-charged with an inverse charge compared to the actual charger to prevent the analyzed particles being charged due to the generating system itself. Multiple spectra from both samples were analyzed with constant EDB and emission detection parameters, which are listed in Table S3, including the used components. The optical components are described in more detail by Järvinen et al. (2014).

3. Results

3.1. Achieved charging states

As in earlier studies (e.g., Järvinen et al. 2017; Kaminski et al. 2012) the charge distribution was found to closely follow a log-normal distribution. Therefore, the
geometric mean was selected as a suitable indicator for the charging efficiency, rather than arithmetic mean. The geometric mean values were defined from the log-normal fit functions for each measured particle size. Figure 5 shows an example of the measured charge distribution for 0.760 μm particles, the lognormal fit, and both of the mean charge values.

Both of the mean values can be found from (Table S1) and from Figure 6 for all of the measured particle sizes. The geometric standard deviation of the log-normal fit function is also included in the Table S1. Additionally, a power function was fitted to the geometric mean results:

\[
n(d_p) = \begin{cases} 
228 \cdot d_p^{1.20}, & d_p \leq 0.86 \, \mu m \\
247 \cdot d_p^{1.72}, & d_p \geq 0.86 \, \mu m
\end{cases}
\] (7)

When comparing Equation (7) to the geometric mean values, mean absolute percentage error of about 3.9% and root-mean-square deviation of about 34 were calculated.

The geometric mean value results were compared to computational charging states using Equations (1) and (2). From the geometrical (charging zone diameter \(D = 13 \, \text{mm}\), charging zone length \(x = 10 \, \text{mm}\)) and experimental (flow rate \(Q = 2 \, \text{lpm}\), corona discharge current \(I = 20 \, \mu A\)) parameters used in the measurements, an \(Nt\) product was approximated as \(1.5 \times 10^{17} \, \text{sm}^{-3}\). This was then applied to Equations (1) and (2), which were furthermore fitted with the geometric mean values of the measurement. The best fit (using the linear least-squares fit method) for the electric field strength \(E\) with the chosen \(Nt\) product value was \(7.7 \times 10^{5} \, \text{V} \, \text{m}^{-1}\), which is in good agreement with the field simulations presented in Figure 1. When comparing the fit function with the experimental results, mean absolute percentage error and root-mean-square deviation of about 5.2% and 34 were calculated, respectively. A comparison to charging states of earlier studies of Hewitt (1957), Liu and Pui (1977) and Unger, Boulaud, and Borra (2004), is presented in Figure 6, including the fit functions presented above.

During the charging state measurements, the electrical losses were estimated to be approximately 50%. Such losses are typical in this type of a charger, since the high final charge number—and thus high electrical mobility—is reached using an intense electric field, which also strongly drives the charged particles toward the grounded outer cylinder of the charger. Altogether, the charger works efficiently on its purpose: to reach a high charging state for large particles with a simple design. The reached arithmetic mean charge values are comparable to values reported by Hewitt (1957). The field simulations conducted during the charger design were in good agreement with the theoretically estimated (Equations (1) and (2)) charge values. In the next subsection, the power function (Equation (7)) was used when studying the electrodynamic balance with achievable charging states.

### 3.2. Electrodynamic trapping limits

The simulation results for the electric fields and the particle trajectories are presented in more detail in the
The main result of the simulations is a threshold AC-voltage $V_{\text{AC}}$:

$$V_{\text{AC}} = \frac{z_i}{ZC} \sqrt{\frac{3gZC_2}{2C_0}},$$

which is the voltage required for a stable particle trajectory in the EDB. In Equation (8), $Z$ is the electrical mobility and $z_i$ the initial position of the particle at the positive $z$-axis, $g$ is the standard acceleration due to gravity and $C_0$, $C_1$ and $C_2$ are geometrical constants of the EDB electrode configuration, defined in Equations (S7) and (S8). Equation (8) was verified with 10,000 particle trajectory simulations using the measured charge distribution and random but realistically ranging other parameters, also presented in more detail in the SI.

Interestingly, it turns out that the AC-field frequency or the particle density do not affect the stability. The independencies may be due to the lack of strong interaction between the AC-field and the charged particle, leading to relatively slow speeds and accelerations in the oscillation: the particle is constantly moving at the thermal velocity in the AC-field, independent of the frequency or particle mass.

The experimentally defined AC-voltages required for a stable particle trajectory are plotted as a function of the calculated threshold value from Equation (8).

That the experimental results with a constant AC-frequency are in a good agreement with the results from particle trajectory simulations. However, the AC-frequency slightly affected the threshold voltage with a relation of about $V_{\text{AC}} \propto f^{0.1}$, which was not predicted by the simulations.

With the equation for the threshold voltage one can predict whether there is a realistic chance of stably trapping a particle with a known electrical mobility and initial position. Straightforwardly, the minimum charge number needed to trap a spherical particle can be calculated as a function of particle diameter. However, one must assume the initial position of the particle to calculate the threshold. Equation (8) predicts that when the particle is driven to the exact focus spot, the AC-voltage needed to keep the balance should approach zero. This is obviously not the case due to external forces and unidealities in the real-world electrode configuration. Instead, even if the particle seems to be at the exact focus spot, it might slowly drift away from it if the AC-voltage is too small. The physical process behind the phenomena might be that the external forces or unideal field shape deviate the particle from the focus, drifting it to a region where the focusing AC-field can no longer compete with the growing DC-field.

It was experimentally estimated that the threshold amplitude AC-voltage required to stabilize the particle...
in the focus spot is equal to the voltage value required to drift the particle toward the focus spot from an initial distance of \( z_i = 0.7 \text{ mm} \). This initial position was used together with Equation (8) to estimate the minimum charge number needed for a stable balance as a function of particle size. The results are shown in Figure 8 for AC amplitude voltages of 1, 2 and 4 kV.

It can be seen from Figure 8 that for particles with a charge value defined in Equation (7), the minimum particle size that can be stably balanced with \( V_{AC} = 1 \text{ kV} \) is about 3.5 \( \mu \text{m} \) in diameter and with \( V_{AC} = 2 \text{ kV} \) about 1.3 \( \mu \text{m} \). The 4 kV amplitude AC-voltage was experimentally estimated to be the safe maximum operating amplitude that does not lead to an electric breakdown with the used EDB configuration. With the maximum amplitude, the achieved charging states should be enough to overcome the trapping limit due to the DC-field. As already mentioned, external forces such as the convective airflow may also disturb the trapping procedure as the particle size gets smaller (e.g., Aardahl et al. 1997).

The LIBS analysis does not necessarily require a fully established balance, but a particle slowly drifting through the focus spot is acceptable for successful analysis. Therefore, the analysis could be carried out for 1 \( \mu \text{m} \) particles (measured by an Aerodynamic Particle Sizer, APS 3320, TSI) using voltage amplifiers with a maximum output of 1 kV. Such analysis, however, requires active manipulation of the particle position by adjusting the DC-voltage. The LIBS analysis results from laboratory generated kaolinite aerosols procedure are presented in the next chapter.

### 3.3. Composition measurements

The averaged spectra from both generation methods (wet and dry generation), both divided with the background signal from air are shown in Figure 9. The average full width at half-maximum (FWHM) value for the peaks was 0.17 nm, meaning that the splitting of the aluminum ground state could be easily detected.

Residual particles from a wet generation source reach up to the Rayleigh limit charge (Järvinen et al. 2014), thus making the trapping efficient even for submicron particles. However, the initial droplet size is usually in the size range of tens of micrometers, (e.g., Berglund and Liu 1973; Järvinen and Toivonen 2016; Udey, Jones, and Farquar 2013), meaning that with a 1 \( \mu \text{m} \) residual particle the possible impurities in the carrier liquid condensate with a factor of \( 10^3 \text{–} 10^6 \) considering mass. Thus, when measuring from a droplet-generated source, the spectrum from “pure” droplet residuals has to be measured as a background reference, as in Saari et al. (2016). If the particle contains only small amounts of the elements also present in the contamination source, it might be challenging to detect them from the background signal. When analyzing...
directly from airborne particles, impurities are not likely to be present, as can be seen from Figure 9.

Effectively, a 100% hit rate (i.e., particle hits/amount of laser pulses) was achieved with the ambient sampling system for particles larger or equal to 1 μm in aerodynamic diameter. The analysis rate was about 1 particle/min at an ambient concentration range of 1–10 particles/cm³, which is of the same order with the timed ablation system presented by Maeng et al. (2017) for the concentration range in question. In continuous-flow systems operating at low concentrations, long waiting times causing pulse laser instability and/or the limited operational cycle of the laser might cause decrease in the hit rate and thus in the analysis speed (Maeng et al. 2017; Manninen et al. 2008; Järvinen, Saarela, and Toivonen 2013). However, for larger (>500 particles/cm³) concentrations, such system provides more particle hits in time unit, compared to the EDB-LIBS. Automated operation of the EDB-LIBS could however lead to an arbitrarily low concentration limit and to faster analysis rate compared to the manual operation.

4. Conclusions
A novel technique capable of analyzing of single particles elemental composition from ambient air and low concentrations (1 cm⁻³) was presented. It has great potential for any applications that require real-time single particle elemental characterization especially for low ambient concentrations. The method is based on electrodynamic balance (EDB) combined with laser-induced breakdown spectroscopy (LIBS). To accomplish ambient electrodynamic trapping of non-precharged particles, an aerosol charger was designed, prepared and characterized. With the known charge distribution, the performance of the EDB could be characterized using realistic charge values. A threshold value for the stable trapping of corona-charged particles was derived numerically and verified experimentally. Still, the main limiting factor of the trapping procedure is the charging state, which diminishes as a function of particle size. Therefore, the lower limit of the ambient EDB-LIBS analysis method is at 1 μm of particle diameter.

Based on the laboratory experiments, the background signal that was present in wet generation method diminished when sampling dry generated particles from ambient air. This phenomena was expected, since an evaporating droplet loses the majority of its mass in pure water, leaving the impurities condensing in the residual with a factor of around 10⁵–10⁶ in mass concentration. When measuring particles trapped directly from ambient air, this interference is virtually eliminated. This improves the sensitivity of the method significantly.

Ongoing and future work with the method consists of automation and finding ways to go further below 1 μm in particle size. Preliminary experimental results stand that amplifying the AC-voltage on the electrodes enables the trapping of sub-micrometer particles, but LIBS spectra from such particles are yet to be collected. Ongoing work also consists of condensation growing the particles before charging them to enhance the charging state closer to the Rayleigh limit. Automated timing of the trapping procedure might enhance the trapping efficiency further to arbitrary low concentrations, since the only limiting factor concentrationwise at the moment is the manual operation of the trapping. Once automated, the technique is to be prepared to a field-deployable instrument for ambient measurements.

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Towards elemental analysis of ambient single particles using electrodynamic balance and laser-induced breakdown spectroscopy

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1 On the charge distribution measurement of a monodisperse aerosol

The electrical mobility $Z$ of a spherical aerosol particle is defined by

$$ Z = \frac{neC_c}{3\pi\eta d_p}, \quad (S1) $$

where $n$ is the number of elementary charges $e$, $C_c$ is the Cunningham slip correction factor, $\eta$ is the viscosity of the medium and $d_p$ is the particle diameter (Flagan 2011). A differential mobility analyzer (DMA) lets particles with certain electrical mobility pass through it, while driving other particles away from the flow with an electric field. When using a closed sheath flow system with the DMA, the electrical mobility of particles that ideally completely penetrate it can be expressed by

$$ Z^* = \frac{Q_{sh} \ln (r_2/r_1)}{2\pi V L}, \quad (S2) $$

which is a function of the geometric parameters $r_1$, $r_2$, $L$, sheath flow rate $Q_{sh}$ and the voltage $V$ set on the DMA’s middle electrode (Flagan 2011). If the particles under analysis are monodisperse considering particle diameter, the charging state of particles passing through the DMA at a known voltage can be calculated straightforwardly from $S1$ and $S2$ leading to

$$ n = Q_{sh} \frac{\ln (r_2/r_1)}{2\pi V L} \frac{3\pi\eta d_p}{eC_c}. \quad (S3) $$

When stepping through voltages and recording the concentration that passes the DMA, one can directly obtain the shape of the charge distribution’s logarithmic density function $\frac{dN}{d\log(n)}$ from the concentration values: The DMA’s transfer function $\Omega(Z)$ is ideally a triangle in the $Z$-space, going to one at $Z^*$ and to zero at values of $Z^* (\frac{Q_{sh} - Q_{a}}{Q_{sh}})$ and $Z^* (\frac{Q_{sh} + Q_{a}}{Q_{sh}})$. When calculating the difference $\Delta \log Z$ of the logarithms of the zero points of the transfer function, it remains the same with constant flow rates. It is clear from $S1$ that $\Delta \log(Z)$ and $\Delta \log(n)$ are directly proportional, leading to a conclusion that $\Delta \log(n) = \alpha$ is also constant. The total concentration $N_{\text{meas}}$ that passes through the DMA is the density function times the transfer function integrated over $\log(n)$:

$$ N_{\text{meas}} = \int_0^{\infty} \frac{dN}{d\log(n)} \Omega(\log(n))d\log(n). \quad (S4) $$
If the product $\Omega(\log(n)) \cdot \frac{dN}{d\log(n)}$ is approximated as a triangle, then the integral, which is the area under the curve at a logarithmic scale (see fig. S1), becomes

$$N_{\text{meas.}} = \frac{dN}{d\log(n)} \frac{\alpha}{2},$$

where $\alpha$ is the difference in $\log(n)$ of the DMA’s transfer function triangle’s endpoints. The measured concentration after the DMA is thus directly proportional to the density function $\frac{dN}{d\log(n)}$.

Figure S1: Illustration of the charge distribution measurement calculations from a monodisperse aerosol with a charge distribution. The product of the density function and the transfer function is approximately a triangle with a constant width $\alpha$ in the log($n$) scale. Therefore the integral value, which is the concentration value recorded after the DMA, is directly proportional to the density function $\frac{dN}{d\log(n)}$.

The achieved charge values using the charger presented in chapter ”Aerosol charging” are presented in Table S1. The table includes geometric and arithmetic mean values of the measurement and the geometric standard deviation of the log-normal fit function of the measurement points.
Table S1: The geometric and arithmetic mean values of the charge distribution for the measured particle sizes, including the GSD-values of the log-normal fit of the charge distribution.

<table>
<thead>
<tr>
<th>Particle diameter $d_p$ (µm)</th>
<th>Geometric mean of $n$ (e)</th>
<th>GSD of the log-normal fit</th>
<th>Arithmetic mean of $n$ (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.60</td>
<td>119</td>
<td>1.22</td>
<td>177</td>
</tr>
<tr>
<td>0.75</td>
<td>169</td>
<td>1.20</td>
<td>222</td>
</tr>
<tr>
<td>1.00</td>
<td>224</td>
<td>1.25</td>
<td>430</td>
</tr>
<tr>
<td>1.30</td>
<td>354</td>
<td>1.19</td>
<td>563</td>
</tr>
<tr>
<td>1.70</td>
<td>615</td>
<td>1.21</td>
<td>1080</td>
</tr>
<tr>
<td>2.25</td>
<td>1040</td>
<td>1.23</td>
<td>1660</td>
</tr>
<tr>
<td>3.00</td>
<td>1680</td>
<td>1.20</td>
<td>2350</td>
</tr>
<tr>
<td>3.80</td>
<td>2460</td>
<td>1.24</td>
<td>4140</td>
</tr>
</tbody>
</table>
2 Electric field and particle trajectory simulations in the electrodynamic balance chamber

Recalling and rearranging the force equation (5) from the main text:

\[
\frac{d^2z}{dt^2} + \frac{3\pi \eta d_p}{m C_c} \frac{dz}{dt} - \frac{q E_{AC}(z)}{m} \cos(\omega t) - \frac{q E_{DC}(z)}{m} + g = 0, \\
(S6)
\]

and acknowledging that the DC-field is a function of \( z \), the field strength terms \( E_{DC}(z) \) and \( E_{AC}(z) \) remain unknown in the equations (5 & S6). Thus, the fields were studied along the \( z \)-axis with simulations of the electrode configuration.

Figure S2 (a) and (b) include the simulated and fitted (amplitude) electric field strengths of \( E_{AC} \) and \( E_{DC} \) in the electrodynamic balance (EDB) along the symmetry axis \( z \). Part (c) of fig. S2 includes the \( x \)- and \( y \)-components of the \( E_{DC} \) field. The ground potential electrodes are removed from the figure (c) since they enclose the inner electrodes, but they were present in the simulations.

**Figure S2:** Simulations of the electric field in the EDB: (a) and (b) consists the AC- and DC-field strengths at the \( z \)-axis with a few voltage values, including the linear and polynomial fits. The shape of the DC-field at the proximity of the \( z \)-axis is illustrated in (c), including only the components perpendicular to the axis.
It was noticed that \( E_{\text{DC}}(z) \) follows a second-order and \( E_{\text{AC}}(z) \) an approximately linear polynomial function at the \( z \)-axis in a few millimeter proximity of the focus spot (fig. S2 (a, b)). Also, due to the \( x \)- and \( y \)- components of the DC-field, the \( z \)-axis acts as an attractor above the focus point and as a repeller below it, as can be seen from part (c) of fig. S2. Since both of the fields are also linearly dependent on the voltages set to the electrodes, following equations could be derived for them at the \( z \)-axis:

\[
E_{\text{AC}} = 2V_{\text{AC}} \frac{C_1}{z_0^2} z 
\]  \hspace{1cm} (S7)

\[
E_{\text{DC}} = V_{\text{DC}} \left( \frac{C_0}{z_0} + \frac{3C_2}{z_0^3} z^2 \right) 
\]  \hspace{1cm} (S8)

in which there are geometrical constants \( z_0, C_0, C_1, \text{ and } C_2 \). \( V_{\text{AC}} \) is the AC-field amplitude voltage and \( V_{\text{DC}} \) is the voltage that is set on the lower electrode, while the upper electrode is on a voltage of \(-V_{\text{AC}}\). Equations (S7 and S8) are approximations to the analytical solution of the field inside an EDB, presented in detail by e.g. Aardahl et al. (1997) and Hartung and Advesian (1992). Thus, the constants are defined in a similar manner. In the approximation, the constant \( C_2 \) defines the spatial dependency of \( E_{\text{DC}} \). To our knowledge, the dependency has not been studied as a cause of instability for particles with a low charging state before. From the simulations, values for the geometric parameters with the used electrode configuration (Heinisch et al., 2009) were estimated to be: \( C_0 = 0.477, C_1 = 0.523 \) and \( C_2 = 0.449 \).

Assuming that the DC-component can be readily tuned in a way that it cancels out the effects of gravity at the exact focus (\( z = 0 \)) spot, \( V_{\text{DC}}^* \) becomes, with a straightforward calculation:

\[
V_{\text{DC}}^* = \frac{z_0 mg}{qC_0} 
\]  \hspace{1cm} (S9)

When applying \( V_{\text{DC}}^* \) and the equations of the electric fields (eqs. (S7 and S8)) to the force equation (eq. (5 & S6)), we obtain

\[
\frac{d^2 z}{dt^2} + \frac{3\pi \eta d_p}{m C_e} \frac{dz}{dt} - \frac{2qV_{\text{AC}} C_1}{m z_0^2} \cos(\omega t) z - \frac{3C_2}{z_0^3 C_0} g z^2 = 0 
\]  \hspace{1cm} (S10)

All terms in eq. (S10) are either geometrical constants or known functions of \( z \). Therefore, the particle’s trajectory could be solved numerically to inspect the stability at the \( z \)-axis. The assumption of a particle staying at the axis is valid at points above the focus point, since for a charged particle the DC-field acts as an attractor above the focus point and as a repeller below it (fig. S2 (c)). Therefore, the initial position of the particle was set to a positive random value between 0 and 1 mm in the simulations. This way the assumption of the particle staying in the symmetry axis would hold in the experimental part of the investigation as well.

A multitude of simulations were conducted with varying parameter values defining eq. (S10). The particle trajectories were classified as either stable or unstable, depending on the location of the particle: if the final position was closer to the focus spot than the initial, a trajectory was considered stable. By variating the used simulation parameters one at a time, a threshold AC-voltage which is needed for a
stable trajectory was found, of the form

\[ V_{AC}^* = \frac{z_0}{ZC_1} \sqrt{\frac{3g_zC_2}{2C_0}}, \]  

which is the main result from the numeric analysis.

Equation (S11) was verified with 10000 simulations using randomly varying parameter values presented in Table T2. Some of the trajectories are presented in fig. S3. Part (a) in the figure contains example particle trajectories with 4 unstable and 5 stable ones and part (b) contains a quantity of simulation results with randomly varying parameters. From the latter figure panel it can be seen that the threshold equation is in good agreement with the test simulations: When \( V_{AC} \) is smaller than the calculated threshold voltage, the trajectory ends up unstable and when \( V_{AC} \) is larger than the calculated threshold voltage, the trajectory ends up stable.

**Figure S3:** A few examples of the simulated particle trajectories (a) and verification simulations of the threshold voltage of eq. (S11) (b). In both figures, a trajectory is considered stable if the final position is closer to the focus spot than the initial. In (a), the oscillation due to the AC-field is averaged out, leaving only the average position of the particle to the trajectory. In (b), trajectories were simulated with random parameters presented in Table T2 and every marker represents a single simulation. The x-axis of part (b) is the threshold voltage value (eq. S11) calculated using the simulation parameters and the y-axis is the amplitude AC-voltage of the simulation in question.
Table S2: Ranges of variation of the parameters used in particle trajectory simulations. The parameters were randomized individually for each simulation in fig. S3(b). The charge number $n$ follows a random log-normal distribution around the geometric mean value from eq. (3), and $\eta_0$ is the viscosity of air at NTP-conditions.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle diameter $d_p$</td>
<td>[0.6; 5] $\mu$m</td>
</tr>
<tr>
<td>Particle charge $n$</td>
<td>$[0.5; 2] \cdot n(d_p)$</td>
</tr>
<tr>
<td>Initial position $z_i$</td>
<td>[0; 1] mm</td>
</tr>
<tr>
<td>AC-field voltage $V_{AC}$</td>
<td>[0; 2000] V</td>
</tr>
<tr>
<td>AC-field strength parameter $\xi$</td>
<td>$[10; 110] \cdot 10^3$ m$^{-2}$</td>
</tr>
<tr>
<td>DC-field strength parameter $C_0$</td>
<td>$[60; 180]$ m$^{-2}$</td>
</tr>
<tr>
<td>DC-field strength parameter $C_2$</td>
<td>$[10; 30] \cdot 10^6$ m$^{-3}$</td>
</tr>
<tr>
<td>AC-frequency $\omega/2\pi$</td>
<td>$[75; 225]$ Hz</td>
</tr>
<tr>
<td>Particle density $\rho$</td>
<td>$[500; 2500]$ kgm$^{-3}$</td>
</tr>
<tr>
<td>Gas viscosity $\eta$</td>
<td>$[0.75; 1] \cdot \eta_0$</td>
</tr>
</tbody>
</table>

3 The equipment used in the EDB-LIBS analysis

The optical and electrical equipment and operating parameters used in the EDB-LIBS analysis are listed in the following table (Table S3).

Table S3: Devices and parameters used in the analysis.

<table>
<thead>
<tr>
<th>Model, manufacturer &amp; location</th>
<th>Physical unit</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Voltage generator</td>
<td>Frequency</td>
<td>100 Hz</td>
</tr>
<tr>
<td>LabView, USB-6363 DAQ-card,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>National Instruments Corp.,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Austin, TX, USA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Voltage amplifiers</td>
<td>AC-amplitude</td>
<td>1 kV</td>
</tr>
<tr>
<td>Model 2210, Trek Inc.,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lockport, NY, USA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spectrometer</td>
<td>Center wavelength</td>
<td>413 nm</td>
</tr>
<tr>
<td>250is, Bruker Corp.,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Billerica, MA, USA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Laser</td>
<td>Aperture slit width</td>
<td>10 $\mu$m</td>
</tr>
<tr>
<td>NT 342/1/UVE, Ekspla Ltd.,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vilnius, Lithuania</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Detector</td>
<td>Pulse energy</td>
<td>5 mJ</td>
</tr>
<tr>
<td>DH340T-18U-E3, Andor Technology Plc., Belfast, UK</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lenses</td>
<td>Diameter</td>
<td>25 mm</td>
</tr>
<tr>
<td>Edmund optics Ltd., Barrington, NJ, USA</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

More detailed description of the optical equipment is presented by Järvinen et al. (2014).
References


Paper 2

Elemental analysis of single ambient aerosol particles using laser-induced breakdown spectroscopy

Heikkilä, P., Rostedt, A., Toivonen, J., and Keskinen, J.

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Elemental analysis of single ambient aerosol particles using laser-induced breakdown spectroscopy

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Analysing the composition of aerosol particles is essential when studying their health effects, sources and atmospheric impacts. In many environments the relevant particles occur in very low concentrations, meaning that their analysis requires efficient single particle techniques. Here we introduce a novel method to analyse the elemental composition of single aerosol particles sampled directly from the aerosol phase using size amplification aided aerosol charging (SAAC), linear electrodynamic quadrupole (LEQ) and laser-induced breakdown spectroscopy. We present results of the charging and focusing efficiencies of the SAAC and of the LEQ, and a proof-of-concept of the analysis method. The proof-of-concept test series was conducted with particle diameters down to 300 nm, sampled directly from the aerosol phase. The method shows unprecedented performance for spectroscopic submicron particle analysis from arbitrarily low concentrations and has exceptional potential for a portable analysis platform for various applications in the field of aerosol research.

Aerosol particles impact human life in a multitude of ways: they participate in cloud dynamics\textsuperscript{1}, cause premature mortality\textsuperscript{1}, transmit diseases\textsuperscript{1} and impair visibility\textsuperscript{4}, for example. Impacts of aerosols are especially difficult to study, when the corresponding phenomena occur at very low particle number concentrations. Such important and timely phenomena include ice nucleation in the atmosphere\textsuperscript{5–7} and the airborne transmission of infectious diseases such as COVID-19\textsuperscript{8–10}. In the atmosphere, the concentration of ice-nucleating particles (INPs) is of the order of a few particles/litre\textsuperscript{9}. Moreover, the emission from the human respiratory tract is of the order of few particles/ccm\textsuperscript{10}. A key factor when studying the types and sources of INPs is their composition\textsuperscript{11–12}. Recent studies have also demonstrated the potential of composition analysis methods in identifying pathogens\textsuperscript{13–14}. As the particles are scarce in both environments, the composition analysis should be conducted on a single particle level.

Composition of aerosol particles can be investigated utilizing collection and subsequent laboratory analysis, which enables acquiring sophisticated data ranging from elemental analysis up to single particle spatial composition information\textsuperscript{15,16}. However, with such analysis, the temporal resolution of the analysis declines and the time delay between collection and analysis may cause measurement artefacts to the results, caused by compounds evaporating and/or condensing on the sample\textsuperscript{17,18}.

An established real-time method to measure the composition of single aerosol particles is aerosol mass spectrometry\textsuperscript{19}, which enables to acquire detailed information with rapid sampling rates. However, mass spectrometry requires a high vacuum, expensive equipment, and relatively heavy data analysis and calibration procedures\textsuperscript{20}. As an alternative, laser-induced spectroscopy methods, such as laser-induced breakdown spectroscopy (LIBS)\textsuperscript{21–23}, have drawn increasing attention during the last decade\textsuperscript{21–23}. LIBS does not require vacuum and can be carried out without complicated sample preparation and at a lower cost compared to mass spectrometry. Airborne particles are exceptionally suitable for LIBS analysis because the matrix is gaseous. Because of the low density of the carrier gas, the matrix effects are significantly lower than with the more traditional solid substrates\textsuperscript{24,25}. However, as LIBS analysis relies on plasma emission induced by a highly focused laser pulse, either the aerosol particle concentration has to be very high\textsuperscript{26} or the particles have to be focused\textsuperscript{22–24}. With state-of-the-art sheath air focusing and timed ablation, sampling rates of tens of particles/minute for single particles are achievable with concentrations above c.a. 500 particles/ccm. However, relatively high pulse energies of above 100 mJ are required to generate a large enough plasma for repeatable particle ablation\textsuperscript{26}.

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In this paper we present a method to focus the particles into the plasma region in a reproducible manner, utilizing size amplification aided aerosol charging (SAAC) and linear electrodynamic quadrupole (LEQ) focusing. With the approach, we introduce the real time elemental analysis of single aerosol particles from ambient air with no lower concentration limit. As the aerosol focusing is conducted with an electric field, laser pulse energies below 10 mJ are adequate to fully ablate the particles. Lower laser pulse energy lightens the pulse laser requirements and leads into better signal-to-background ratios, as the plasma volume decreases. The method shows exceptional potential for applications where particle concentrations are low, such as research on atmospheric ice nucleation or aerosol particles emitted from human respiratory tract.

LEQ-LIBS principle and components

The analysis system is presented schematically in Fig. 1a and in more detail in the Supplementary Fig. 1a,b and the Supplementary Table 1. In SAAC, the sample aerosol first flows through a particle growth tube (Model GTC50, Aerosol Dynamics, Inc.), which consists of a wetted paper wick with three temperature-controlled sections to induce and control particle growing: a cold (10 °C) saturator, a hot (50 °C) heater and a cool (18 °C) moderator. The size amplification occurs in the heater part, as water diffuses from the wick into the aerosol at a faster pace than heat31. As shown in Fig. 1b, the particle diameter after the amplification has a median at about 3 µm. After the size amplification, the aerosol flows through a unipolar corona-discharge based aerosol charger, presented in more detail in earlier research27. As the particles are size amplified, the powerful electric field in the charger causes them to acquire a high electrical charge27 (Figs. 1c and 3). After SAAC, the particles are directed into the LEQ-LIBS chamber through a virtual impactor, which concentrates the large particles into the chamber and omits most of the carrier gas. In the chamber, the particles are dried with a small dry sheath air. As the particles dry and thus decrease in size, their electrical mobility increases rapidly. The increased electrical mobility then enables the quadrupole field to focus the particles into the symmetry axis of the electrodes. Furthermore, the Coulombic repulsion force between the particles causes spacing between them, which ensures single-particle operation.

As a particle moves with the airflow along the symmetry axis (Fig. 1d), it crosses with a CW laser beam (405 nm, 100 mW), perpendicularly focused into the axis (Fig. 2a,b). The 405 nm light scattered by the particle causes them to acquire a high electrical

Characterization methods

SAAC charging performance

The charging states reached by the SAAC were measured using monodisperse DEHS-particles generated by the single charged aerosol reference (SCAR). The detailed measurement setup is presented in Supplementary Fig. 2b. First, the SCAR-generated aerosol was divided into a CPC (3756, TSI Inc.) to monitor the total concentration and into the SAAC to charge the aerosol. The temperatures of the saturator, the heater and the moderator were set on 10 °C, 50 °C and 18 °C, respectively. Then, the size-amplified aerosol was charged using a total electric current of 20 µA and a 2 lpm flow rate in the charger. After the charger, the aerosol was dried and introduced into another CPC (3750, TSI Inc.) through a DMA (3085, TSI Inc.). When scanning voltages with the DMA, the number concentration measured by the CPC is directly proportional to the density function of the particle charge density, as demonstrated earlier27.

As DEHS particles are hydrophobic, isopropanol (IPA) was introduced into the aerosol by driving the aerosol generated by SCAR through a heated IPA container. This procedure caused the DEHS particles to absorb IPA, which is soluble to water. This addition of IPA enabled the size amplification of initially hydrophobic particles in the SAAC27.

LEQ-LIBS performance

The performance of the LEQ-LIBS system was evaluated in terms of hit ratio and analysis speed as a function of aerosol concentration using 300 nm NaCl particles. The measurement setup flowchart is presented in more detail in Supplementary Fig. 2a. In the proof-of-concept phase, the particles were generated using a custom-made bubble generator, which generated bubbles from four 0.5 mm spherical nozzles into a 1-% NaCl water solution. After the generation, the aerosol was introduced into a chamber with a volume of 10 L, which acted as a residence time chamber and a dryer, as dry pressurized air was introduced into it alongside with the sample aerosol. From the chamber, the sample was blown through an AM-241 neutralizer, an impactor with a cut point of about 420 nm and a differential mobility analyser (DMA, 3081A, TSI Inc.), respectively, with a flow rate of 2 lpm. After the DMA, the sample was humidified and divided into a condensation particle counter (CPC, 3776, TSI Inc.) to monitor the concentration and into the SAAC-LEQ-LIBS system for the elemental analysis. The total flowrate into the SAAC was 2 lpm, of which 0.1 lpm was directed into the LEQ through a virtual impactor. When adding the 0.25 lpm dry sheath air into the LEQ, the total flowrate through it was 0.35 lpm. The LIBS spectra were automatically analysed and considered as successful if the signal peak value was 1.5 times the mean of the background value. Additional spectra were analysed from tap water residual particles and Arizona test dust particles.
LEQ focusing efficiency

Particle focusing in the LEQ was evaluated numerically. Electrodynamic balance (EDB) systems have been used in aerosol research for decades, and their performance is also evaluated and documented mathematically. In the following some of the earlier work is applied to the LEQ geometry to provide tools for its particle focusing performance. In the absence of external forces, the force equation for a charged particle in an oscillating electric field is, as Newton's 2nd states:

\[ \sum F = m a \]

where \( \sum F \) is the sum of all forces acting on the charged particle, \( m \) is the mass of the particle, and \( a \) is the acceleration of the particle.

Figure 1. A schematic figure of the LEQ-LIBS analysis. (a) The left side illustrates the aerosol flow path through the system. The aerosol first flows through the size amplification, in which condensed water increases the particle size up to ca. 3 µm, as shown in (b). After the amplification, the aerosol is charged with a unipolar corona discharge charger, which leads to charging states of several thousand elementary charges/particle (c). After the charging, particles are directed into the LEQ, in which an oscillating electric field drives them into the symmetry line, as shown in (d). As a single particle drift through the analysis spot, it is detected with a separate 405 nm CW-laser (omitted from the figure), which triggers an Nd:YAG laser, which then turns the particle and the surrounding gas into plasma with a laser pulse having ca. 7 mJ of energy. As the plasma cools down, an elemental emission spectrum is recorded with a spectrometer and an ICCD camera (e).
where \( d_p, m, q \) and \( r \) are the diameter, mass, electrical charge and the position of the particle, respectively, \( \eta \) is the viscosity of the carrier gas, \( \omega \) is the angular frequency of the oscillating electric field and \( C_c \) is the Cunningham’s correction factor for small particles. As the particles are flowing parallel to gravity in the LEQ, the focusing is only considered in its perpendicular dimensions. Gravity is thus omitted from the equation, leaving

\[
\frac{d^2r}{dt^2} + \frac{3\pi \eta d_p}{C_c} \frac{dr}{dt} - qEAC(r)\cos(\omega t) = m \frac{d^2r}{dt^2},
\]

(1)

The above Eq. (2) is often expressed with dimensionless variables \( Z = \frac{z}{z_0} \) and \( \tau = \frac{wt}{\omega z_0 d_p^2} \), which describe the position along an axis of interest and the number of concurred oscillations in the electric field, respectively. The expression includes parameters \( \delta = \frac{36Q}{C_{lamp}d_p^4} \) and \( \beta = \frac{24QV_{LAS}}{\omega d_p^2 \epsilon \mu_0 d_p^4} \), which describe the drag force and the electric force exerted to the particle, respectively. In the parametrization, \( \rho \) is the density of the particle, \( z_0 \) is the distance from the edge of an electrode into the symmetry axis and \( C_l \) is a geometric constant describing the slope of the oscillating electric field. The parametrization leads to a dimensionless equation

\[
\frac{d^2Z}{d\tau^2} + \delta \frac{dZ}{d\tau} + 2\beta Z\cos(2\tau) = 0,
\]

(3)

from which stability areas with respect to \( \delta \) and \( \beta \) can be numerically calculated. If the position of the particle along the \( Z \)-axis is solved (MATLAB, The MathWorks Inc.) and its average plotted as a function of the dimensionless time \( \tau \), one can easily see that it follows an exponential function with a negative exponent (Supplementary Fig. 3):

\[
Z(\tau) = Z_0 e^{-\tau/\tau_f}.
\]

(4)
In Eq. (4), \( Z_0 \) is the initial position of the particle and \( \tau_{ef} \) is a factor describing the time it takes for a particle to drift into the focus spot, i.e., relaxation time in an electrodynamic balance. By solving the differential Eq. (3) with a multitude of different parameter \( \delta \) and \( \beta \) values and comparing the results with Eq. (4), the relaxation time can be found to be (Supplementary Fig. 4):

\[
\tau_{ef} = \left( 1 + \frac{4}{\delta^2} \right) \left( \frac{\delta^3}{2\rho} \right).
\]

If written in the context of Eq. (2), including dimensions, (4) and (5) can be described as

\[
r(t) = r_0 e^{-t/\tau_{ef}},
\]

and

\[
\tau_{ef} = \left( 1 + \frac{\rho^2 C_d^2 q^2 \omega^2}{324 \eta^2} \right) \frac{81 \pi^2 \rho^4 Z_0^4}{\rho C_f V_d q^4 C_e^2} = \frac{z_0^4}{2mBZ^2 C_f V_d}. \quad (7)
\]

In Eq. (7), \( B \) and \( Z \) are the mechanical and electrical mobilities of an aerosol particle, respectively. The Eqs. (4)–(7) can be used to evaluate the focusing efficiency of an EDB in general. This can be helpful in designing a focusing system on which the charging states of the particles is not initially high.

Equations (6) and (7) were used to estimate the time that is needed for the particles to drift within a 20 µm radius of the focus line. This radius can be assumed as a threshold for a successful LIBS analysis in the LEQ, as demonstrated in earlier research with similar optical setup and LIBS pulse energy\(^{27}\). Results of the calculated times are shown in Fig. 5. In the calculations, \( C_1 = 0.77 \) was determined from electric field simulations (COMSOL Multiphysics, COMSOL Inc.) inside the LEQ with the used electrode configuration, presented in supplementary Fig. 1b. The charging states were set to 2000, 4000 and 8000, which are in the modes of grown particles’ charging states of Fig. 3, the amplitude AC-voltage was set to 2 kV, frequency to 1 kHz and particle sizes from 100 nm to 10 µm with unity as density. Also, as a comparison, similar calculations are shown for particles charged without the size amplification, but instead with charging states following the equation for ungrown particles with the same aerosol charger\(^{27}\).

Characterization results

Size amplification aided aerosol charger (SAAC)

The final charging states of the particles charged with SAAC are shown in Fig. 3. As a comparison, the charge distributions for ungrown particles charged with the same corona charger are also shown. The charge distributions have been normalized due to their area in the logarithmic scale. As can be seen from the figure, the size amplified particles reach a similar charging state of a few thousand elementary charges/particle, regardless of their initial size, and the ungrown particles’ charge distributions are more separate. When processed as log-normal, mean geometric charge values of 3600, 4000 and 4400 were fit to the distributions for initial sizes of 0.4 µm, 0.6 µm and 1.1 µm, respectively. A small difference in the final size of the grown particles might cause the slight difference between the final charging states. However, the smaller particles still have a larger electrical mobility due to their smaller diameter and are thus easier to focus in the LEQ.

The median diameter of the particles after the water condensation is found to be ca. 3 µm, as shown in Fig. 1b. The final charge is slightly larger when compared with the charging states without the size amplification at the same size\(^{27}\). This is likely due to the different polarity of the charger, as negative ions used in this study have a larger electrical mobility than positive ones.

LEQ-LIBS proof-of-concept and performance

The results from the LEQ-LIBS performance analysis are shown in Fig. 4. As can be seen from the figure, the hit ratio for ambient concentrations below 1 particle/ccm is well above 90%, and the analysis speed has an optimum at around 1 particle/ccm and is of the order of 10 particles/min. With higher concentrations, the particles experience electrical interference between each other and cause false triggers, which leads into decrease in the hit ratio and analysis rate. Thus, with such concentrations, the aerosol should be diluted before analysis. These results act as a proof-of-concept for the analysis method.

The analysis rate at about below 0.1 particle/ccm is restricted by the small particle concentration itself and between 0.1 and 1 particles/ccm by the LIBS laser pulses: the plasma formation causes a pressure wave into the surrounding gas, which drives the nearby particles away from the focus line, thus requiring some settling time before the next pulse (Supplementary Videos 2, and 4). However, the analysis rate may be improved with more sophisticated temporal flow pattern, i.e., increasing the flow rate temporarily after every pulse or with a faster sheath flow. This could bring the particles unaffected by the previous pulse closer to the analysis spot faster, letting the analysis flow more rapidly.

A radius of 20 µm from the focus line is assumed to be the threshold for a successful LIBS analysis, as experimentally demonstrated in earlier research with a similar optical setup and pulse laser energy\(^{27}\). Figure 5 presents results from numerical simulations of the time it takes for a particle to reach the radius with the used electrode setup and several different charging states. When interpreting Fig. 5, it may well be assumed that to be able to efficiently analyse submicron ambient particles with LEQ focusing, the particles must be size amplified before the charging process. However, particles with a diameter greater than ca. 4 µm are charged with respect to their primary size, as the size after the “amplification” would be below that. According to the simulation, the charge these large particles acquire without amplification is high enough for the analysis. The maximum charge limit,
namely Rayleigh limit is also presented in the figure for water droplets. As a particle evaporates, it might cross the Rayleigh limit and lose some of its charge via Coulombic fission with a negligible decrease in mass39. As can be seen from the figure, the Rayleigh limit ultimately prevents reaching arbitrarily low relaxation times for the smallest particles.

In addition to the hit ratio and focusing performance analysis, example spectra from Arizona test dust and tap water residual particles were analysed. The spectra can be seen in Fig. 6, which contains the average successful spectrum of the performance analysis test series (a), an example spectrum from a single Arizona test dust particle (b) and an example spectrum from a single tap water residual particle (b). The particle diameters corresponding to the spectra were 300 nm (Fig. 6a) and ca. 1–3 µm (Fig. 6b,c).

**Figure 4.** Hit ratio and analysis rate results for 300 nm NaCl particles. The hit ratio (successful emission spectra/laser shots) and analysis rate are presented as a function of ambient particle concentration. As can be seen, the hit ratio is above 90% for concentrations < 1 particle/ccm, which is also the optimal concentration considering the analysis rate. Above that, the hit ratio and analysis rate decrease, which is due to electric interference between the particles in the LEQ. The hit ratio error bars are 95% confidence intervals calculated with the Clopper–Pearson method assuming a binomial distribution38.

**Figure 5.** Drifting times toward the focus spot. A radius of 20 µm from the focus line was used as a limit that enables the analysis to succeed, as presented in earlier work37. The blue line represents the charge values obtained without the size amplification27 and the black crosses the experimental charge values from the SAAC analysis. As can be seen from the figure, particles below a few µm in diameter must be size amplified before charging to reach a reasonable relaxation time.
Conclusions

A novel method to efficiently control initially neutral submicron aerosol particles in an electrodynamic field to conduct laser-induced breakdown spectroscopy was introduced. LIBS analysis of ambient submicron particles from such low concentrations has not been accomplished in earlier research. The performance of the method was presented on a proof-of-concept level with 300 nm NaCl particles, and LIBS hit ratios of above 90% were achieved for concentrations of under 1 particle/ccm. The optimal particle concentration was found to be of the order of 1 particle/ccm, for which the analysis rate was ca. 10 particles/min. Also, performances of the separate parts of the method were evaluated. The charging states reached with the size amplification aided aerosol charger (SAAC) system were shown to be of about a few thousand elementary charges, which was shown to be enough—and necessary—for efficient focusing of submicron particles in the electrodynamic quadrupole system.

The next major step of development is to conduct measurements of initially unknown aerosols, which requires a wideband emission spectroscopy instrument, such as an echelle- or a multi-channel spectroscope. This is because with a narrow-band emission spectroscope only one or two elements can be monitored at a time, and it is unlikely that the single particles contain just that element. Furthermore, analysing the proportional shares between different elements in single particles is crucial when classifying them. As the test series was conducted with initially neutral aerosol particles sampled from the aerosol phase, the analysis method is expected to work for unknown aerosols as well.

With the SAAC, consistently high charging states were attained. The platform enables the use of any electrodynamic balance for ambient, initially neutral particles without the need for droplet generation and charging systems. Most important development area in SAAC would be to decrease the electric particle losses in the charger, as they were found to be above 70%. Optimising the flow path in the charger, such as adding a sheath flow from the outer tube would prevent the particles from drifting towards the outer walls. Should the particle losses decrease, the analysis rate in the LEQ-LIBS would be higher with a lower initial aerosol concentration.

The analysis rate, which in the current state has a maximum at 10 particles/minute, is also a field of further development. In this study, the most limiting factor was the shockwave caused by the LIBS laser pulse, which drove the nearby particles away from the focus. The effect of the shockwave could be limited by increasing the flow rate in the chamber momentarily after each pulse or by striving towards smaller pulse laser energies by lowering the wavelength, which would possibly lead to a smaller shockwave in the air.

The numerical method to calculate the relaxation time in the LEQ, or an electrodynamic balance in general, may be considered a practical tool to estimate the focusing efficiency for initially uncharged aerosols. The focus in earlier research has mostly been in highly charged droplets\(^{36}\), with only few exceptions\(^{40}\). However, the simulations have been only partially experimentally verified with measurements\(^{37}\).

In summary, the method shows great performance for the online elemental analysis of aerosol particles on a single particle level from arbitrarily low concentrations. Such aerosol environments occur, for example, in atmospheric ice nucleation studies and human respiratory particle studies. Also, the capability to analyse from low concentrations enables the size-segregation of the aerosol population before the analysis without losing all
the resolution power. As the used laser pulse energies were below 10 mJ, the method also shows great portability potential.

Data availability
The datasets and simulation scripts generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

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References
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Author contributions
All the authors participated in the planning of the analysis method and of the measurements. P.H. conducted the measurements, data analysis, numerical modelling and wrote most of the article. A.R. provided technological support and know-how on matters including electronics and signal processing. J.K. and J.T. participated in the writing process.

Competing interests
The authors declare no competing interests.

Additional information
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Correspondence and requests for materials should be addressed to P.H. or J.K.

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Author Correction: Elemental analysis of single ambient aerosol particles using laser-induced breakdown spectroscopy

Paavo Heikkilä, Antti Rostedt, Juha Toivonen & Jorma Keskinen

Correction to: Scientific Reports https://doi.org/10.1038/s41598-022-18349-8, published online 29 August 2022

The original version of this Article contained errors. The particle size in Figures 3 and 5 was incorrectly calculated. This slightly affected the particle charge. The corrected particle sizes are 400 nm, 600 nm and 1100 nm and the corrected particle charge distributions are shown in the figures.

The original Figure 3 and 5 and accompanying legends appear below.

As the result, in the Characterization results, under the subheading 'Size amplification aided aerosol charger (SAAC)',

“When processed as log-normal, mean geometric charge values of 2300, 2900 and 3700 were fit to the distributions for initial sizes of 0.3 µm, 0.5 µm and 1.0 µm, respectively."

now reads:

“When processed as log-normal, mean geometric charge values of 3600, 4000 and 4400 were fit to the distributions for initial sizes of 0.4 µm, 0.6 µm and 1.1 µm, respectively."

The original Article has been corrected.
**Figure 3.** Charge states achieved with the SAAC. The dotted lines present charging states for dry particles, and the solid lines for the size amplified particles. The legend entries present the dry particle diameter. As can be seen from the figure, the dry size has some effect on the final charge of the grown particles. All the curves have been normalized due to their area in the logarithmic scale.

**Figure 5.** Drifting times toward the focus spot. A radius of 20 µm from the focus line was used as a limit that enables the analysis to succeed, as presented in earlier work\(^3\). The blue line represents the charge values obtained without the size amplification\(^2\) and the black crosses the experimental charge values from the SAAC analysis. As can be seen from the figure, particles below a few µm in diameter must be size amplified before charging to reach a reasonable relaxation time.
Supplementary information for:

Elemental analysis of single ambient aerosol particles using laser-induced breakdown spectroscopy

Paavo Heikkilä, Antti Rostedt, Juha Toivonen, Jorma Keskinen
Description of the supplementary videos:

In all the videos, the particles are 300 nm in diameter and the particle material is NaCl.

Video 1 presents the LEQ focusing with aerosol concentrations below 1 particles/ccm and the interference between particles when the concentration is too large.

Video 2 presents the LEQ-LIBS analysis in action with a concentration of about 0.1 particles/ccm.

Video 3 is a slow motion video of the analysis of a single particle.

Video 4 presents the LEQ-LIBS analysis, when the particle concentration is too large. The shockwave generated by the laser pulse can be clearly seen in the video.
Supplementary Figure 1: a CAD-drawing of the LEQ chamber (a) and a schematic figure of the electrodes (b). The highly charged aerosol is directed into the chamber from the inlet on the top, and the copper electrodes carry out the focusing. The monitoring and optical analysis is conducted through the 25.4 mm threaded channels, which contain either lenses or simple windows. The distance between two adjacent electrodes is 10 mm measured from the midpoints.
**Supplementary Table 1: Detailed information about the devices and physical parameters used in the analysis.**

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Supplementary Figure 2: The measurement setups in the proof-of-concept measurement (a) and in the charge distribution measurement (b).
Supplementary Figure 3: An example simulation of the flow path of a particle along an axis of interest inside an EDB. As can be seen from the figure, the averaged path follows an exponential function defined by the equation in the legend.

Supplementary Figure 4: An example simulation series of the relaxation time. The y-axis contains the quotient when dividing a fitted relaxation time value (the red line in Supplementary Figure 4) with the predicted value from equation (5) or (7). The agreement is excellent, meaning that the equations have great prediction power of the relaxation time in an EDB, according to the simulation.
Paper 3

Analysis and classification of individual ambient aerosol particles with field-deployable laser-induced breakdown spectroscopy platform

Heikkilä, P., Rostedt, A., Toivonen, J., and Keskinen, J.

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Analysis and classification of individual ambient aerosol particles with field-deployable laser-induced breakdown spectroscopy platform

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ABSTRACT
Studying the elemental composition of aerosol particles on a single particle level is of importance when determining the internal and external mixing state of the aerosol population. We present a field-deployable platform for the elemental analysis of ambient single particles using laser-induced breakdown spectroscopy (LIBS). The platform utilizes a wide-band spectrometer for simultaneous multi-element detection and size-amplification-aided aerosol charging (SAAC) for efficient particle focusing via a linear electrodynamic quadrupole (LEQ). Carefully designed emission collection system allows minimization of the plasma background emission, which allows us to use short gate delays for increased yield of analyte emission. Performance evaluation with a set of well-defined salt aerosols show excellent capability in determining the relative mass percentage and absolute mass of elements spanning multiple orders of magnitude on a single particle level. Limits of detection for Mg, Na and K were determined to be approximately 2 fg, 40 fg, and 70 fg, respectively. An outdoor aerosol sample was analyzed in the size range of 1–3 μm in diameter, and the particles were classified into distinct categories based on their elemental composition. The maximum analysis speed is about 20 particles per minute and the minimum detectable particle size is, depending on the constituent elements, about 300–800 nm. Emission signals of Al, B, C, Ca, Cu, Fe, K, Mg, Na, Si, and Ti were detected during the measurements of generated or outdoor aerosols.

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1. Introduction

Ambient air contains a complex mixture of aerosol particles both indoors and outdoors. Aerosols have multiple significant impacts on society: they affect the climate (Ramanathan et al. 2001), cause health issues and premature mortality (Lelieveld et al. 2015), act as disease transmitters (Zhang et al. 2020) and impair visibility (Singh and Dey 2012). Measuring the chemical composition of these particles at a single-particle level is of importance when studying their external and internal mixing state (Riemer et al. 2019; Shen et al. 2019), monitoring for airborne toxic (Lu et al. 2017; Martin et al. 2007) or pathogenic (Li et al. 2023) agents, or determining their sources (Xu et al. 2018). Being able to measure ambient single particle composition is of crucial importance in ice-nucleating particle measurements (Hoos and Mohler 2012; Paramonov et al. 2020).

The elemental and chemical composition of single particles may be resolved using offline or online methods. Offline methods include sensitive tools to analyze the chemical composition up to the spatial level of a single particle (Fletcher et al. 2011). However, microscopy requires sample preparation and transportation and heavy-duty equipment. Obviously, the temporal resolution of aerosol composition is limited with offline techniques, and sample transportation may introduce artifacts to the analysis (Turpin, Huntzicker, and Hering 1994). To analyze single aerosol particle composition online, the most established technique is single-particle mass spectrometry (Riemer et al. 2019; Gemayel et al. 2016; Gard et al. 1997). With it, many organic and inorganic molecules and elements may be detected in real time with portable instruments. However, mass spectrometry requires a good vacuum, expensive equipment, and heavy data analysis.
An alternative for the online elemental analysis of aerosols at a single particle level is laser-induced breakdown spectroscopy (LIBS) (Singh and Thakur 2020; Zhang, Zhang, and Li 2021). LIBS enables the analysis of particles directly from the ambient air without the need for a vacuum or intricate data processing. Thus, multiple systems have been developed to analyze aerosol particles with LIBS in the last decades (Sipich et al. 2022; Heikkilä et al. 2022; Maeng et al. 2017; Hybl et al. 2006; Carranza et al. 2001). As mentioned in our previous paper (Heikkilä et al. 2022), the main challenge in LIBS is to focus the particles into the same volume as the focused pulse laser beam, which may be in the order of a few hundreds of cubic micrometers (Järvinen and Toivonen 2016). To overcome this challenge in the case of ambient aerosol analysis, several approaches have been presented by previous authors. These include using a high laser pulse rate and relying on a probability of hitting a particle every now and then (Carranza et al. 2001), focusing them with sheath air (Park, Cho, and Kwak 2009) and using timed ablation (Maeng et al. 2017; Hybl et al. 2006), or charging and focusing with an electrodynamic balance (Heikkilä et al. 2020). In our approach, we employ a size-amplification aided aerosol charger (SAAC, Heikkilä et al. 2022) to charge the ambient aerosol, followed by focusing them onto a narrow path using a linear electrodynamic quadrupole (LEQ). The focusing enables to guide the particles through a focus spot of a triggered LIBS pulse, generated by a 355 nm Nd:YAG laser (Litron Nano SG 150-10, Litron Lasers Ltd.) The triggering signal is acquired utilizing a 405 CW laser (RLDE405M-100-5, Roithner LaserTechnik GmbH), combined with a photomultiplier tube (H5773-03, Hamamatsu Photonics K.K.). Both lasers are first brought into the same optical path utilizing a dichroic mirror (69-200, Edmund Optics Ltd.) The triggering signal is acquired utilizing a 405 CW laser (RLDE405M-100-5, Roithner LaserTechnik GmbH), combined with a photomultiplier tube (H5773-03, Hamamatsu Photonics K.K.). Both lasers are first brought into the same optical path utilizing a dichroic mirror (69-200, Edmund Optics Ltd.) and then tightly focused on to the particle using a 12.7 mm diameter plano-convex lens with a 50 mm focal length (LA4765-A Thorlabs Inc.).

In comparison to earlier developments, this paper presents a field-deployable platform, wideband spectral analysis, and an enhanced sample rate for aerosol analysis. In addition, the optical chamber and the LEQ dimensions have been revised. Schematics of the SPAA and the revised optical arrangement can be found from Figures 1 and 2, respectively. Online supplementary information (SI) Figures S1 and S2 include photographs of the mobile platform.

The SPAA is built on a 98 cm x 65 cm x 60 cm (length x width x height) rack case (3RR-11U24-25M, SKB cases) with a removable rack. This allows for installation of the optics inside the case to ensure eye-safe operation on field measurements. As shown in Figure 1, the optics are assembled on an optical table (MBH4560/M, Thorlabs Inc.) mounted at the bottom of the rack. The aerosol is guided into the case from an 8-mm inlet hole at the top. As the power source of the pulse laser is mounted inside the case, active cooling is introduced with a fan from the side of the case. An additional rack for the SAAC, electronic equipment and for the operating laptop was built on top of the case from aluminum profile. Total maximum
The dimensions of the platform are 1.2 m x 1.0 m x 0.6 m and its weight is about 80 kg.

The optical system revision includes a new emission collection system, more comprehensive plasma-particle monitoring, and tilted viewing angles into the focus spot, rather than keeping everything on a single viewing plane (Figure 2). The atomic emission is collected with a concave UV-enhanced aluminum mirror \((f = 19 \text{ mm}, D = 25.4 \text{ mm})\) and focused into a fiber bundle with a custom-made achromatic triplet lens (Thorlabs LA5370, LA5763 & LC4252). The fiber bundle is then divided into 3 branches leading to a multi-channel USB-spectrometer (Multi-Channel AvaSpec-ULS4096CL-EVO, Avantes B.V.) operating at wavelengths of 200–450 nm, 450–700 nm, and 700–1000 nm (Figure 3). The plasma-particle positioning is monitored utilizing 2 CMOS cameras with different viewing angles to ensure focusing on all dimensions. To enhance the particle focusing efficiency (as calculated in Heikkilä et al. 2022), the LEQ dimensions were downsized to 1.0 mm diameter stainless steel rods separated by 7.0 mm (center-to-center) from adjacent rods.

The emission collection from the analyte particle is illustrated in Figure 3. As the optical power of the laser exceeds the breakdown value of the gas (in the order of 100 MW), it initiates plasma formation to the focus spot. After the initial breakdown, the plasma starts to absorb the laser irradiance in a cascaded manner, which leads to plasma formation toward the...
opposite direction of the laser propagation, as illustrated by Thakur and Singh (2007, p. 11). If the particle is at the exact focus spot of the pulse laser and the emission is collected from the same spot, majority of the plasma is not seen by the spectrometer. Thus, the presented arrangement minimizes the background signal of the plasma irradiation, which mainly originates next to the focus spot. Furthermore, this enables to use short gate delay times with minimal interference from the plasma, which is brightest right after the laser pulse. Using short gate delays combined with long integration time is beneficial in capturing most of the emission from different elements within a single measurement, as they have varying optimal emission time windows (Rai and Thakur 2007).

2.2. Spectral data processing

When analyzing initially unknown aerosol particles with LIBS, special consideration needs to be given to the emission signal processing. To reduce the noise from ambient gas emission and the dark noise of the detector, each analyzed spectrum was first subtracted by a background spectrum originating from an average of 30 laser shots without particles present. As each particle only provides one spectrum, conventional multi-spectral averaging methods cannot be directly applied, which leads to a larger noise especially in weak emission peaks. Furthermore, when analyzing initially unknown samples, no prior knowledge about the peak’s wavelengths’ is available.

Considering the boundary conditions in the provided data, we utilized a peak finding algorithm and Gaussian fits to find the peaks and determine their areas and wavelengths in each spectrum. In practice, peaks with prominence of 60 counts were located from each spectrum, and the Gaussian fit was used to define the wavelength and area of the peak after the background and baseline subtraction. The wavelengths of the found peaks were compared to a library of known elements and their corresponding LIBS emission wavelengths. If a wavelength of a peak was within 0.1 nm from a known emission line, its area was used as the emission signal for that element. As most elements divide their emission into multiple energies and our measurement system can operate in a wide range of wavelengths, total peak area per element could be constructed by summing the areas of each peak of the element under inspection or monitoring a single prominent peak with least known interference from other elements. Accepting multiple peaks into the analysis increases the total analyzed peak area, but also increases the noise between subsequent spectra, as that is also multiplied with this approach. A comparison between multipeak and single peak analysis was conducted for several elements and no significant increase in resolution power was obtained when using multiple peaks. As per the results of the comparison, further data analysis was proceeded with only a single emission line per element. The analyzed elements and their wavelengths can be found from SI Table 1. Traditionally in LIBS studies, a Lorentzian fit is used as a fit function, but when processing the data acquired with the SPAA, it became quickly evident that Gaussian fits provide better results in terms of regression analysis parameters and fit stability.

2.3. Laser energy and plasma location optimization

The energy of the pulse laser and the spatial location of plasma with respect to the particle under analysis were investigated to maximize the emission signal. Two different aerosols (Salt solution of MgSO4, NaCl and KCl; kaolinite dust (Al2Si2O5(OH)4)) including five analyte elements (Mg, Na, K, Al, and Si) were utilized to optimize the signal on a wide spectral range and with different types of elements.

Figure 4 presents the measurement setup in detail for both salt aerosol and dry aerosol analysis. The same measurement scheme was used in the measurements presented in the following subchapters, excluding the ambient aerosol analysis, in which the sample aerosol was outdoor air. The samples of the salt solution were size-selected by a Differential Mobility Analyzer (DMA 3081 A, TSI Inc.) to a size of 1 μm and the kaolinite aerosol was sampled at a size of 1.25 μm. The size of the aerosol population was monitored utilizing an Aerodynamic Particle Sizer (APS 3321, TSI Inc.) after the size classification, and the aerodynamic sizes were found to be approximately 20% larger than the classification size of the DMA. The geometric standard deviations were approximately 1.2 for both samples. Only a small amount of multiply charged particles were detected, as the original size distributions had smaller median diameters than the classification size and thus the relative abundance of larger particles was low. The salt aerosol consisted of the same mixture as in sample number 1 in Table 1, i.e., the proportional masses of the analyzed elements were Mg: 9.6% Na: 38.5% and K: 51.9% in a dry particle.
### 2.4. Multielement aerosol analysis

Several test aerosols were generated to characterize simultaneous multi-element analysis. An approximation of proportional number content (n-%) of measurable elements in single particles was derived utilizing the Boltzmann plot method (Bousquet et al. 2023) and the NIST LIBS database (Kramida, Olsen, and Ralchenko 2019). In the following subsections the tests are described in more detail.

#### 2.4.1. Estimation of number share of elements in generated aerosols

In addition to the bubble generated salt samples, a brush aerosol generator (RGB-1000, Palas GmbH) was utilized to disperse kaolinite, Arizona test dust (ATD, ISO 12103-1, Powder Technology Inc.) and ISO12103 PT1 (ISO 12103-1:2016 A1, Particle Technology Ltd.) test dust. Their spectral footprints were analyzed and compared to each other. As the ATD contains calcium, its emission peaks were used to evaluate the electron temperature of the plasma with the Boltzmann plot method. This temperature was then utilized to acquire data from the NIST LIBS database to calculate initial factors for peak area normalization to estimate the number shares (n-%) of detected elements within single particles. Furthermore, data from the salt particle analysis presented in the next subchapter was used to evaluate optical throughput for the 3 spectrometers. This throughput data was combined with the initial factors acquired from the NIST database for the number share analysis.

#### 2.4.2. Analysis performance with well-defined salt particles

For a more in-depth study of the resolving power considering relative and absolute mass composition of an element per particle, several salt solutions with magnesium sulfate, sodium chloride and potassium chloride were prepared with different relative concentrations. Table 1 includes the concentrations of the salts and calculations of their cations’ (Mg, Na, and K) relative masses in the final aerosol particle. The initial hydration state of MgSO₄ used in the solutions was found to be 4 by measuring the weight loss of a sample after heating it to over 250 °C.

The elements were chosen to provide spectral signal simultaneously into a wide spectral range, as Mg, Na and K have the most prominent peaks at around 280, 590, and 770 nm, respectively. The selection rules and the differences in electron structures of the elements cause some electron transitions to happen more likely than others. Moreover, differences in the plasma temperature and free electron density cause some excited states to be more populated than others, causing the transition probabilities to be dependent on the environment, i.e., the parameters of the plasma. Thus, the atomic emission line intensities within and between the elements may vary many orders of magnitude (Thakur 2007). This variation can be readily observed from Figure 5a. Thus, the solutions were prepared to reach a comparable signal for each of the elements.

---

**Table 1.** The samples used in the resolving power analysis.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Mass of salt in H₂O solution (g/300 ml)</th>
<th>Proportional mass in dry particle</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MgSO₄</td>
<td>NaCl</td>
</tr>
<tr>
<td>1</td>
<td>4.99</td>
<td>5.02</td>
</tr>
<tr>
<td>2</td>
<td>0.60</td>
<td>1.51</td>
</tr>
<tr>
<td>3</td>
<td>0.30</td>
<td>10.38</td>
</tr>
<tr>
<td>4</td>
<td>1.20</td>
<td>5.40</td>
</tr>
</tbody>
</table>
elements (Mg, Na, K), which leads to Mg having by far the lowest concentration in the particles.

Four particle diameters (0.8, 1.0, 1.25, and 1.5 μm) were used to be able to assess the sensitivity as a function of absolute element mass per particle. Each particle sample-size combination measurement consists of ca. 200 spectra. In addition, each sample underwent bulk X-ray Fluorescence (XRF, M4 Tornado Plus, Bruker Nano GmbH) analysis for comparison. The XRF sample was prepared by drying a few centiliters of the solution on a petri dish and the analysis was conducted on crushed crystals within a 10 mm x 8 mm area. In general, with XRF, limits of detection in the ppm range are achievable, but the sensitivity decreases with lighter elements (Marguí, Queralt, and de Almeida 2022). The values are comparable to the limits achievable with LIBS (Fabre et al. 2018).

2.5. Ambient aerosol analysis and classification

A set of ambient aerosol particles was measured, sampled directly from outdoor air, using a sampling tube through the laboratory window. The sampling site is located in the campus area of Tampere University, in a sub-urban area of Hervanta in Tampere city (61°27′00.0″N 23°51′25.0″E, ~140 m above sea level). The wind was blowing from the vast forest area from the south. A virtual impactor (VI) with a dp50 value of 1 μm was utilized to concentrate the supermicron particles. After the VI, the aerosol
was classified using a DMA (Model 8021, TSI Inc.) set to sample 1.2 μm particles. Due to a high probability of multiple charging in the neutralizer of the DMA, the size distribution was monitored with an APS (3321, TSI Inc.) and verified to stay between 1.0 and 3.0 μm. A total of 313 particles were analyzed and classified into 5 categories based on their elemental composition. The example sample was measured on 2.8.2023 during 15.10–15.50.

3. Results

3.1. Laser energy and plasma location optimization

Figure 6 presents the main results of the pulse laser energy optimization. Considering pulse laser spatial focusing, the best spectral consistency and signal was achieved when the laser was directly focused into the particle, as illustrated in Figure 3. This means, in practice, that the particle is located at the very edge of the plasma toward the direction of beam propagation, as the plasma forms from the focus spot into the opposite direction. Plasma-particle focusing has been studied before with similar results by Järvinen and Toivonen (2016) for Pb analysis. However, with substantially higher energies, other researchers have demonstrated increase in some molecular emission signals if the plasma is focused slightly off the particle and let spread into it (Purohit, Fortes, and Laserna 2017).

Figure 6a includes the median peak area as a function of energy for peaks of Mg, Na, K, Si, and Al. Each marker represents at least 200 single particle spectra. The (b) panel includes a measure for the relative variation between single particle spectra, defined as the median area value from panel (a) divided by the interquartile range (IQR) of all the measured peak areas for the energy/element combination. Robust indicators such as median and IQR were chosen instead of mean and standard deviation because multiple charging of the particles cause a few significant outliers to the data. The outliers are still relatively rare, as the initial size distribution has a median in much smaller sizes than the setpoint of the DMA.

As described earlier, Mg, Na, and K were measured from 1.0 μm particles containing a salt solution sample 1 (Table 1), and Si and Al were measured from dry-generated 1.25 μm kaolinite (Al₂Si₂O₅(OH)₄) particles. Most of them had the highest signal output in the regime close to 4 mJ. The exception was magnesium, which peaked a few millijoules higher. The relative variation of single particle spectra was minimized around 5 mJ for all the elements. To maximize the signal output and minimize the inter-particle signal fluctuations, pulse laser energy of 4.5 mJ were used for the upcoming measurements of the following sections.

As described in Section 2.4, the LIBS emission intensities may vary multiple orders of magnitude for similar analyte masses. This is mostly noticeable by the variation between magnesium and the rest of the elements in Figure 6a: even though the proportional mass of magnesium in a dried particle was less than 10% compared to the other two (Na and K) alkalis, roughly an order of magnitude higher peak areas were measured. Furthermore, the masses of Si and Al in a single particle were multiple times higher than the masses of Na and K, yet similar peak areas were measured for all of them, even when integrating through the counts from all their emission peaks. The anions of the salts (S, Cl) were not observed at all.
3.2. Multielement aerosol analysis

3.2.1. Spectra from generated particles and n-% normalization

Example spectra from generated aerosols and of the background measurement are presented in Figure 7. The x-axis is divided into relevant areas of the spectra, showing ranges of 220–320 nm, 385–405 nm, 580–600 nm, and 750–790 nm. The samples consist of salt sample 4 (Table 1), Arizona test dust (ATD), kaolin dust and ISO test dust. Most of the inspected elements have their emission peaks in the range of spectrometer 1, but sodium and potassium are only visible at spectrometers 2 and 3, respectively.

In the background measurement, oxygen and nitrogen of ambient air are clearly visible. Furthermore, even with the subtraction of background from the
for all the four example aerosols. In the figure, the measured median values of peak areas are compared to the masses of elements calculated from the original salt solution and of the particle size. The error bars on the y-axis include the interquartile range (IQR) of the peak areas for the particle size/sample combination and on the x-axis the IQR of the masses of the analyte elements in single particles. The masses of elements and their IQRs in single aerosol particles are derived from the original salt concentrations, the median particle size of the DMA and the deviation of the particle diameter measured by the APS. Particle size of 1.0 μm of sample 4 was chosen as a calibration sample, from which a simple linear calibration factor $I_a$ was derived for each element $z$, relating the peak area $I_a$ to the analyte mass $m_a$, $I_a = I_0/m_a$. The calibration sample is marked in all the panels (a)–(d) for all the elements.

Using the calibration sample, estimations of analyte mass/particle could be calculated for the other samples. These estimations are shown in Figure 5b. The vertical error bars present the IQR of the measured masses and the horizontal error bars are again the IQR of the particle mass in the aerosol population. As can be seen, the linear calibration predicts the masses quite well over a wide range of masses. Furthermore, most of the variance in the mass measurement may be interpreted to originate from the variance in the aerosol distribution, as the error bars have almost identical lengths in both axes. Therefore, the measurement spectra can be used to determine the apparent plasma temperature. For this, singly ionized calcium emission lines of ATD sample were used, as the method requires two or more lines with a sufficient (a couple of eV) spread of upper level energies. With the method, an average plasma temperature of approximately 11600 K (corresponding to 1.0 eV/kB in atomic units) was derived from the results. This temperature was approximated to be valid for all the other elements as well. With the temperature, the NIST LIBS database was utilized to acquire reference spectra for all the elements and the same spectral analysis was conducted to all of them as was conducted to the measurement spectra. These peak areas were then used as normalization factors to conduct an approximation of the relative number concentration of elements within single particles. Furthermore, correction factors for different spectrometers were added to the approximation from the results of the next section. A few example compositions normalized with the method are presented in Figure 8 for all the four example aerosols. As can be seen, the salt aerosol, kaolinite, and ISO Test dust yield relatively homogenous composition, but the ATD has more heterogeneity between the particles. A similar observation of heterogeneous distribution of minerals in single ATD particles has also been noted by Vlasenko et al. (2005).

3.2.2. Analysis performance with well-defined analyte particles

Well-defined salt solutions with different compositions of Mg, Na and K were aerosolized and size-selected with multiple particle sizes. The particles were analyzed with the SPAA and compared to the original solute masses and bulk material XRF analysis. Figure 5 includes the results from all the particles over all the sizes (0.8 μm – 1.5 μm, $n = 3465$). Each marker includes spectra from at least 200 measurements, excluding the XRF measurements, which were acquired from a bulk sample.
lines as predicted by the Boltzmann distribution and the spreading of the emitting gas causes a decrease in optical throughput, as the image size exceeds the spectrometer slit width.

The same calibration sample (sample 4, particle size 1.0 μm) was also used to relate the relative fractions of peak areas to the relative fractions of analyte elements with a linear constant defined with \( \frac{I}{I_a} = \eta a \frac{m}{M} \). Using the constant \( \eta a \), the measured mass fractions are shown as a function of the actual mass fractions of the solutions in Figure 5c. These values were also divided with the actual mass fraction and plotted on a linear scale in panel (d). Furthermore, the results from the XRF analysis are shown in panels (c) and (d). As can be seen from the panel (d), the LIBS measurements mostly stay within 25% error in determining the mass fractions of known elements in the measured particles, even in the < 1% concentration range for magnesium. The XRF measurements have over 50% error in concentrations below 15%, but for the > 30% concentrations, both measurements yield good results.

An approximation of the limit of detection (LOD) was evaluated for elementary mass as the smallest mass that produced a signal for over 75% of the single particle spectra. These values were found to be about 2 fg, 40 fg and 70 fg for Mg, Na and K, respectively. However, for K, no values were measured below this definition and thus the LOD is probably smaller. Furthermore, the densities of the particles were calculated by comparing the particle size values measured by the APS and the classification size of the DMA and were found to be approximately 1.3 times smaller than excepted from the salt compositions. Thus, the particles probably still contained some water or hollow cavities, as has been reported before by Cheng, Blanchard, and Cipriano (1988). Thus, the LOD values are most likely somewhat smaller than presented, but we have adopted a conservative approach and report them without correction for this effect.

3.3. Ambient aerosol analysis and classification

A total of 313 spectra were acquired during the 40-min sampling period. A total of 13% of shots were misses or included undetectable elements, and the rest could be classified and underwent the same n-% normalization routine as described in Section 3.2. With the sample data, it became evident that a few elemental footprints are constantly repeated. Thus, these spectra were classified into categories presented in Figures 9 and 10. The categories are “Salt particles” (Na, Mg, Ca), “Biological particles” (C, trace amount of K and Ca), “Dust particles” (Si, Al, Fe) and “Carbonaceous particles” (only C). Thorough criteria for classification into a certain group are presented in Figure 11. The criteria were chosen to automatically categorize the particles while avoiding single particles being classified into multiple groups and maintaining compositional homogeneity within the groups. The categories are based on the elemental compositions of different particle types presented in the literature: The “Salt particles”—category is based on Seinfeld and Pandis (2016, p. 354), presenting the composition of sea salt particles. The “Biological particles”—category is based on the abundance of silicon in the particles accompanied by other crustal elements, as presented by Usher, Michel, and Grassian (2003).

In Figure 9, the first few spectra from each category are shown as a similar n-% bar plot as in Figure 8, utilizing the normalization method described in chapter 3.2. The Boltzmann plot method was applied for calcium-rich particles and yielded the same temperature of 11600 K (1.0 eV/k_B) as in the earlier analysis for generated aerosols. A single example spectrum from each group is presented in Figure 10.

An interesting finding about the spectra of carbon-containing particles is the prominence of carbon’s emission line at 229.7 nm (Figures 10b and c). It originates from a doubly ionized state and should thus appear at much higher plasma temperatures than calculated with the Boltzmann plot method. The discrepancy between the observed and excepted emission is likely due to the plasma not being in LTE conditions, as the emission collection period (gate width) is long (10 μs), and the gate delay is short (100 ns). Within

![Figure 9. Normalized example compositions from the outdoors aerosol measurements. As marked into the figure, the particles are divided into four main categories due to their spectral footprints. Each bar stack represents a single particle, and the colors (patterns) indicate measured elements.](image-url)
the gate width, the plasma undergoes a transition through high temperatures and electron densities into lower ones. Thus, the peaks of carbon from different ionized states appear at different times, but as they are integrated into a single spectrum, they seem to conflict with the apparent temperature acquired using the Ca emission lines. However, carbon was the only element showing such evident discrepancy between the apparent temperature and the emission line profile acquired from NIST LIBS database. For the normalization of C, we decided to use a different temperature (21,000 K, i.e., 1.85 eV/kB) for reference spectrum acquisition to better match the perceived and expected line profile.

When comparing the biological and carbonaceous spectra in Figure 9, the difference seems to be minimal. However, from Figure 10, the difference is obvious. This is due to the emission intensity of carbon is still, with the elevated temperature, expected to be at least an order of magnitude smaller than for the others. Thus, even with clearly visible peaks in the raw data spectrum, the n-% of Mg, K and Ca are normalized to be small in the biological particle group.

Figure 10. Example single particle spectra from the four categories of the outdoor aerosol measurement. Due to wideband operation, multiple elements could be resolved simultaneously from each particle, which enables the particle classification.

Figure 11. The relative fractions of the particle categories in the outdoor aerosol sample. Most particles were classified into the Salt category (28%), followed by Biological and Dust (20% each). 7% Included only carbon and 11% were unclassified. The unclassified particles consisted mainly of Na-rich (6%) and Ca-rich (4%) particles.
Figure 11 illustrates the proportional fractions of the particle types defined earlier. The most abundant types were Salt (28%), Dust (20%) and Biological (20%) particles. 8% of the particles were only C. 11% of the particles were unclassified, of which particles with Na-rich and Ca-rich composition consisted of 10% in total. 13% of the spectra were classified as missed, meaning that no known elements were detected. It should be noted that the aerosol was size separated prior to the analysis with a virtual impactor with a cut point at 1 µm and a DMA sampling at 1 µm. Thus, the sample is not representative of the total aerosol, but gives insight to the local aerosol population in the 1 µm–3 µm size range, as measured with the APS. Furthermore, as the analysis is dependent on successful charging of the aerosols, which is dependent on the condensation growth with water, some bias might be caused by the growth efficiency. For example, hydrophilic aerosols such as salts grow relatively easily, and hydrophobic aerosols such as pure DEHS particles don’t grow at all (Asbach et al. 2017). However, few atmospheric particles are as hydrophobic as the DEHS particles.

The classification categories are based on prior knowledge of aerosol particle types (Seinfeld and Pandis 2016; Usher, Michel, and Grassian 2003; Heldal, Norland, and Tumyr 1985; Saari et al. 2016), but have not been verified with, for example, microscopy imaging. It should be noted that this is the first study of wideband LIBS for ambient outdoors aerosol classification, thus there might be discrepancies in the classification. However, there are several arguments that might justify these categories. For the salt particles, utilizing the HYSPLIT data from NOAA archive (Stein et al. 2015) to trace back the trajectory of the local outdoors airmass, it was noted that it had traveled above the Baltic Sea within a few hours before arriving to the measurement location. As the sea is a common source of salt aerosols, it could act as an obvious source for the abundance of the category. The dust particles are easily classified due to the abundance of Si, Al, and Fe (Usher, Michel, and Grassian 2003), and during summertime, the source could be either local or remote. Biological particles are expected to be present during summer, as the biological activity in the surrounding nature is high. Furthermore, previous studies have presented the presence of K and Ca in bacteria. The authors acknowledge this as the most uncertain classification, as particulate carbon combined with trace elements might originate from other sources as well, such as biomass or fossil fuel burning or lubricant oils. However, the abundance of Ca and K combined with the lack of other metallic compounds in the particles would suggest that they are of biological origin (Park and Kim 2005; Yatkin and Bayram 2007; Jahn et al. 2021).

4. Conclusions

In this study, the Spectroscopy Platform for Ambient Aerosol analysis (SPAA) was presented. Its capability for simultaneous multi-element analysis of single aerosol particles sampled directly from the surrounding air was demonstrated and its analytical performance was evaluated with test aerosols and a sample of outdoors aerosol. The transportability was confirmed with field campaigns with results being published later. The sampling rate was found to be in the order of 10 particles/min and the optimum concentration in the order of 1 particle/ccm. The maximum concentration for successful particle analysis is approximately 10 particles/cm³. Above this, the aerosol must be diluted. The limit is due to the electric interaction between particles interfering successful focusing, leading to missed laser pulses. This phenomenon is discussed and demonstrated in more detail in Heikkilä et al. (2022). When comparing the sampling speed of ca. 10⁴ analyzed particles/day to other methods gathered by Riemer et al. (2019), the SPAA is faster than usual microscopic single particle methods (10³–10⁴ particles/day) but slower than many single particle mass spectrometers (10²–10⁶ particles/day). Thus, an important future research area would be to further increase the analysis speed to achieve better sampling statistics, comparable to those of the single-particle mass spectrometers.

The liner electrodynamic quadrupole (LEQ) focusing and the optical system for conducting single-particle LIBS was revised from our previous work. With the revised LEQ, the particles are focused more efficiently without compromising the optical throughput, as the focusing rods are smaller and their relative distance is downsized. The new optical chamber enables for accurate monitoring of the focusing of the trigger laser, the plasma, and the particles from all dimensions. This is of great practical importance to be able to line the lasers and the emission collection system in the most efficient manner. Furthermore, the emission collection system enables to use short gate delays in the LIBS analysis, which was experimentally verified to increase the throughput of the elementary radiation. As the emission is collected from a perpendicular angle of the plasma at its very edge, only a minimal amount of the plasma irradiation ends
up to the spectrometer, thus it does not shade and absorb the emission from the analyte particle.

The SPAA showed excellent performance in measuring the proportional fractions of the generated salt aerosol, exceeding the resolution power of the laboratory XRF analysis. Furthermore, with a simple linear calibration, it could resolve the mass content in single particles in a decent manner, spanning over multiple orders of magnitude in elementary mass. The detection limits for Mg, Na, and K were also evaluated experimentally, and were found to be about 2 fg, 40 fg, and 70 fg, respectively. The wideband spectral resolution enables simultaneous observation of multiple elements on a single-particle basis. Thus, the particles of the outdoor aerosol sample could be divided into distinct categories based on their elementary composition. The sample consisted of 313 particles sampled during a 40-min period.

This research paves the way for multiple directions of the aerosol-LIBS instrument development and LIBS research in general. The optical chamber enables the simultaneous addition of other spectroscopic methods to the system, such as fluorescence and Raman (Saari et al. 2016; Sivaprakasam, Hart, and Eversole 2017). These methods could enable the analysis of the molecular structure and the biological origin of the particles. Furthermore, adding research effort to minimizing the particle losses from the condensation growth assisted aerosol charger (SAAC) system and pre-focusing the aerosol flow into the LEQ chamber could dramatically increase the sample rate from even smaller concentrations. Moreover, the unique nature of the emission collection enables the use of short or even zero gate delays, which is not yet a widely studied region of LIBS analysis.

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Disclosure statement

The authors report that there are no competing interests to declare.

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Data availability statement

All the reported data is displayed in this article.

References


Supplementary material for

Analysis and classification of individual ambient aerosol particles with field-deployable laser-induced breakdown spectroscopy platform

P. Heikkilä, J. Keskinen, A. Rostedt, J. Toivonen

Table 1. Used emission lines for the detection of different elements.

<table>
<thead>
<tr>
<th>Element</th>
<th>Al</th>
<th>B</th>
<th>C</th>
<th>Ca</th>
<th>Cu</th>
<th>Fe</th>
<th>K</th>
<th>Mg</th>
<th>N</th>
<th>Na</th>
<th>O</th>
<th>Si</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength (nm)</td>
<td>396.15</td>
<td>206.64</td>
<td>229.69</td>
<td>393.33</td>
<td>213.62</td>
<td>259.92</td>
<td>766.49</td>
<td>279.58</td>
<td>746.85</td>
<td>589.01</td>
<td>777.40</td>
<td>251.60</td>
<td>334.95</td>
</tr>
</tbody>
</table>
Figure 2. A view into the rack case with the optical components.
Ambient Single Particle Composition Measurement with Laser-Induced Breakdown Spectroscopy

PAAVO HEIKKILÄ