Size-resolved analysis of fine and ultrafine particulate matter by laser-induced breakdown spectroscopy

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In emissions originating from industrial processes, elemental concentration characteristically depends on particle size. Therefore, not only is the average chemical composition of the particles in the focus of interest but also their size-dependent composition. For industrial applications such as on-line process control, a system using laser-induced breakdown spectroscopy (LIBS) is developed providing the analysis of particulate matter directly in an air stream with a short response time to changes in elemental composition. By using a co-flow in addition to the aersosol flow the time resolution of the system can be enhanced. Investigations are undertaken concerning properties of the laser plasma, the analysis of monodisperse and polydisperse aerosols with regard to the relative elemental concentration and the mass concentration of the particles. The system can be calibrated to either total elemental concentrations or relative compositions. The signal response to a variation of elemental concentration as well as to the particle mass concentration show kinds of saturation effects. Temporal plasma evolution for CaCl₂ particles and pure argon are investigated. Different decay times for argon and the particle matter depending on the origin of lines within the plasma are observed. Electron density and temperature are determined using Ca emission lines to describe the temporal evolution of the plasma state for the particle analysis. It has been observed that the electron density increases rapidly for plasma temperatures above 10 000 K. Size-resolved analyses of particles in the size range from 20 nm up to 800 nm are carried out. It has been found that the signal response correlates with the mass distribution of the particles.

Introduction

The analysis of airborne particulate matter in the fine (0.1–2.5 μ m) and ultrafine (<0.1 μ m) size range has become an important issue since such particles have been recognized to significantly affect human health. In particular the small particles intrude deeply into the lung so that toxic compounds are directly absorbed by the organism.^{1,2} Therefore, the knowledge of the size-dependent composition of airborne particles is essential to assess health risks. In addition, analysing the chemical composition as a function of particle size is important for process control, combustion and ambient air pollution monitoring.³⁻⁷ In this case, the analysis can identify particle emitting processes and sources.⁸

During the last few years, a number of studies have successfully demonstrated the use of laser-induced breakdown spectroscopy (LIBS) for the analysis of aerosol particles.⁸⁻¹⁸ While standard analytical methods like mass-spectrometry, *e.g.* ICP-MS, are time-consuming, LIBS is a fast method that can be automated and applied on-line and on-site. Some of the works concern the analysis of particles sampled on filter substrates^{8,13,14} fractionated in size classes by an impactor, and a subsequent LIBS analysis is undertaken in the lab. For on-line applications,

^a*RWTH* Aachen University, Chair for Laser Technology (LLT), Steinbachstr. 15, 52074 Aachen, Germany. E-mail: nadine.strauss@ilt. fraunhofer.de; Fax: +49 241 8906 121; Tel: +49 241 8906-0 ^bFraunhofer Institute for Laser Technology, Steinbachstr. 15, 52074 Aachen, Germany this approach is not adequate; hence, there is a need to analyse aerosol particles directly in an air stream. In this regard, D. Hahn and co-workers have investigated the use of LIBS for aerosol particle analysis in a number of studies^{15–18} dealing with aerosol sampling statistics, conditional data analysis and plasma-particle interaction.

This work presents fundamental studies to develop a system for size-dependent aerosol analysis directly in an air stream with regard to industrial applications. For on-line process-control, there is a need for a fast multi-element analysis with a fast response-time of the system. Here, we present the development of a measurement system comprising a Paschen-Runge spectrometer with rapid multi-channel electronics enabling fast reactions to changes in the chemical composition of particulate matter. We focus on basic investigations of the system behaviour, which are necessary for its calibration. Compared to the analysis of solid samples, the calibration is more complex in this case since it can be influenced by both the element concentrations in the particles and the total mass of particulate matter in the aerosol stream.

Additionally, the measurement process is influenced by the size of the individual particles, the carrier gas and the particle location within the plasma.^{19–21}

This study focuses on the effect of the particle mass concentration and the relative elemental concentration. The temporal plasma evolution of the analyte response of particle matter and gas-phase species is compared. Electron density and temperature are derived as a function of time. The system behaviour is investigated for the analysis of monodisperse and polydisperse aerosols under different measurement conditions.

Experimental

Aerosol sampling

Artificial aerosol is nebulized by an aerosol generator (AGK-2000, Palas, Germany) using N_2 into droplets up to 2 µm diameter. The aerosol is then guided *via* a diffusion dryer by using of N_2 as a carrier gas into a measurement chamber to provide a stream of solid particles ranging between 20 nm and 800 nm in particle diameter. The generator can produce aerosol of different elements by nebulizing different salt solutions. In this study we restrict the analysis to the elements calcium and sodium. It can be assumed that the composition of the dried particles equals the composition of the dissolved material.

To provide size-resolved measurements a commercially available SMPS (= Scanning Mobility Particle Sizer) (TSI, USA) is used to fractionate particles by size. The SMPS system comprises a DMA (differential mobility analyser) model 3080L and a CPC (condensation particle counter) model 3785. The DMA separates particles in a gas stream in a size range from 10 nm to 1000 nm aerodynamic diameter. Due to their electrical mobility, which is inversely proportional to their size, particles are fractionated by size, depending on the electrostatic field strength of the DMA and the sheath gas flow rate, and counted using the CPC. By scanning the electrostatic field strength of the DMA and simultaneously counting the particles, an aerosol size distribution is obtained. An example of a particle size distribution given in number and mass concentration is shown in Fig. 1. The particle size was scanned from 19 nm up to 800 nm in 27 logarithmic steps. The measured LIBS signal is also given and will be discussed in section 'Size-resolved measurements'.

The outlet of the DMA is connected *via* a conductive silicon tube of 2 m length and 5 mm diameter to the measurement chamber of the LIBS set-up, *cf.* Fig. 2.



Fig. 1 Particle size distribution given in number- and mass distribution. The size distribution is scaled in percentage of the total particle number and the total mass, respectively (right ordinate). Additionally the obtained size-dependent LIBS-signal for Ca is plotted and scaled to the left ordinate. The measurement points of the mass concentration are marked with numbers in ascending order.



Fig. 2 Set-up for the LIBS experiments; SP = spectrometer; ES = entrance slit; AF = aerosol flow; CF = co-flow; MC = measurement chamber; LB = laser beam propagating perpendicularly to the plane of projection; SM = spherical mirror; SA = symmetry axis; VP = vacuum pump; a = 50 mm; b = 10 mm.

The gas pressure in the measurement chamber is set to 980 mbar to generate a continuous aerosol flow of 1 lpm through the DMA for all experiments.

The number distribution shows a maximum at 70 nm particle diameter and the mass distribution at about 400 nm. The total number and mass of particles as a sum of all size classes were 4.5×10^6 particles cm⁻³ and 10 mg m⁻³, respectively in this measurement. The dips occurring at 34 nm and 200 nm particle diameter (marked with arrows in Fig. 1) in the number distribution and in the mass distribution are due to two different measurement modes of the particle counter. Aerosols of low particle concentration ($< 2 \times 10^4$ particles cm⁻³) are counted particle by particle (single particle only). In the second mode for particle number concentrations exceeding 2×10^4 particles cm⁻³, the particle number is measured by photometry. The dips appearing in the size distributions are indications of the switching between these measurement modes, *i.e.* single particle counting and photometric mode.

LIBS-setup

For the analysis of the particulate matter in the gas stream a LIBS setup was developed which is shown in Fig. 2.

All experiments are carried out with a flashlamp pumped Q-switched Nd:YAG laser (Continuum Inc., Surelite I-10) at the fundamental wavelength $\lambda = 1064$ nm, a repetition rate of $\nu_{rep} = 10$ Hz and a pulse duration of $\tau_L = 10$ ns. Pulse energies of up to 300 mJ can be used. Analyses are undertaken in a vacuum chamber enabling the use of a co-flow in addition to the aerosol stream (CF in Fig. 2). This co-flow is guided into the chamber *via* two diffuser inlets beside the aerosol inlet which are arranged 50 mm above the aerosol inlet (distance *a* in Fig. 2).

The expanded laser beam (18 mm diameter) is focused into the flow stream perpendicular to the aerosol flow at a distance b = 10 mm downstream of the aerosol exit aperture (2 mm diameter) using an achromatic lens (f = 110 mm). Under these conditions breakdown is initiated by each laser pulse. The generated plasma

light emission is collected by a spherical mirror and focused directly onto the entrance slit of a spectrometer in Paschen-Runge configuration (OBLF, Germany) in which channel electron multipliers are installed for each spectral line of interest. For multichannel measurements, the fast multi-channel integrator electronics (MCI) developed by Fraunhofer ILT is used. The MCI enables time-gated integration and read out of 32 channels in parallel with measurement frequencies of up to 1 kHz.²² To detect spectral line profiles and the whole emission spectrum, an Echelle spectrometer (LLA, ESA 4000) is used in addition. In this case the plasma light emission is collected by a quartz lens into an optical fiber.

Results and discussion

Characterization of the system

To investigate the temporal resolution of the LIBS system, aerosol generated from sodium and calcium chloride solutions was injected into the measurement chamber. Therefore, the pressure in the measurement chamber was held constant to 980 mbar to provide a continuous gas flow of 1 lpm as described above. NaCl and CaCl₂ particles were injected into the gas flow for nearly 10 s in succession. This measurement was carried out without and with the use of an additional argon co-flow. While using the argon co-flow with a flow rate of 5 lpm the pressure in the measurement chamber was still 980 mbar. The time in which the complete gas volume in the chamber is exchanged is estimated to be 8 min without the co-flow. Through the use of the co-flow with a flow rate of 5 lpm, the gas volume is exchanged within approximately 1.3 min.

The plasma emission was observed using the Echelle spectrometer with a delay time of 800 ns and an integration time gate of 30 μ s. Two pulses were averaged which corresponds to a temporal resolution of 0.2 s.

Fig. 3 shows the time-dependent line intensity for the two elements Na and Ca.

Without co-flow the time in which the signal rises between 10% and 90% of the maximum signal amounts to 3.5 s (Fig. 3, left side). In the case of an argon co-flow this value can be reduced to 2.5 s. The 1/e decay time of the signal is in the order of 20 s

without the co-flow, and the duration until the signal can no longer be distinguished from the background is longer than 90 s. In contrast to that, the use of a co-flow reduces this time to approximately 20 s: see Fig. 3, right side. The time when the signal has reached 1/e of its maximum amounts to 10 s.

Using no additional co-flow, the non-averaged line intensity of the calcium line is very noisy whereas with the Ar co-flow this noise level is reduced.

The fast response time is very important for industrial applications to be able to react to changes in the elemental composition. A fast decay time of the system is also important for the temporal resolution and the size resolution concerning SMPS measurements. Assuming a SMPS scanning time of 135 s, which is used here, approximately seven size classes can be swept consecutively.

Plasma evolution

The temporal evolution of the plasma emissions was observed for different argon and calcium lines using the Echelle spectrometer. Measurements were performed with pure argon at 1 bar and with calcium chloride particles in N₂ as a carrier gas. The Ca concentration of the solution was amounted to 0.5 m-%. The emissions were observed using delay times varying from $t_{\text{delay}} = 0.1$ to 25 µs. For delay times up to 4 µs, an integration time gate of $t_{int} = 1 \ \mu s$ was used, while for later periods ($t_{delay} =$ 5, 10, 15, 20, and 25 µs) the integration time was extended to 5 µs to compensate for the weaker line intensity. All other measurement parameters were held constant. A series of 50 single spectra were averaged. The observed emission intensities are shown in Fig. 4 and 5, with the intensities being corrected for the different integration time gates used: i.e. the intensity values obtained for $t_{delay} \ge 5 \ \mu s$ were divided by five. Intensities below 0.1 were not taken into account because of too low SNR. The semi-logarithmic diagram for argon (Fig. 4) exhibits an exponential decay with similar decay times for all Ar lines. Using a linear fit to these data, the decay time τ for each line can be determined following an exponential decay law proportional to $\exp(-t/\tau)$. The decay times obtained from the linear fit curves are listed in Table 1.



Fig. 3 Intensity of a sodium and a calcium line as a function of time without (left side) and with (right side) the use of an additional co-flow into the measurement chamber. Additionally the moving intensity average over two seconds is plotted. The arrows mark the time at which NaCl and CaCl₂ particles were injected into the measurement chamber *via* a tube of 2 m using N₂ as a carrier gas.



Fig. 4 Emission intensity decay measured in pure argon for varying delay times and exponential decay fit curve for the Ar I 706.722 nm and the Ar II 434.806 nm line. Error bars are multiplied by a factor of 100 for $t_{\text{delay}} \leq 10 \,\mu\text{s}$ for better visibility. Negative going error bars are omitted.



Fig. 5 Line intensity decay measured for $CaCl_2$ particles in N₂ as a carrier gas for varying delay times and decay fit line to the Ca II 393.366 nm line for two decay periods and to the Ca II 317.933 nm line. Error bars are multiplied by a factor of 500 for better visibility.

For the four argon lines, a constant exponential decay with about 3 μ s decay time is observed for the full period during which the lines were observable (delays up to 25 μ s).

The lines originating from CaCl₂ particles (Fig. 5) show a different behaviour. For most Ca lines, the decay is not strictly exponential during the whole observation period. However, the curves can be approximated closely by two exponential curves as shown in Fig. 5. While the emission decays rapidly ($\tau < 2 \ \mu$ s) during the first part, the decay is much slower ($\tau > 10 \ \mu$ s) for the following period.

While the two decay times are very similar for different emission lines, the duration of the fast decay clearly depends on the physical parameters of the corresponding atomic or ionic transition. The ground state atomic transition (Ca I 422.7 nm) has the shortest duration (3 μ s) of the fast decay, while it is longer (> 5 μ s) for the ionic ground state transitions (393.366 nm, 396.847 nm) and extends to at least 10 μ s for the higher excited ionic line (317.933 nm). The latter line was not observed for delay times of $t_{delay} > 10 \ \mu$ s any longer and has not reached a slow decay period while it was observable.

The electron density was estimated from the Stark broadening of the Ca II spectral line at 396.870 nm. The profile of the spectral line was approximated by a Voigt profile. The Lorentzian part of the profile was determined by deconvolution. The electron density was then determined using the relation:²⁴

$$\Delta\lambda_{FWHM}^S = 2w\left(\frac{n_e}{10^{16}}\right)$$

where $\Delta \lambda_{FWHM}^{S}$ is the FWHM of the Lorentzian part of the line width, corrected by the instrumental broadening ($\Delta \lambda_{FWHM}^{\prime} = 2.7$ pm), *w* is the electron Stark coefficient listed in the literature²⁵ and *n_e* is the electron density.

Fig. 6 shows the temporal evolution of the electron density which decreases rapidly during the first 3 μ s from 3.2 \times 10¹⁷ cm⁻³ at 100 ns to 0.8 \times 10¹⁷ cm⁻³ at 3 μ s; afterwards it stays constant at approximately 0.5 \times 10¹⁷ cm⁻³.

Analogous behaviour is observed for the time dependence of the electron temperature determined using the Boltzmann plot method.²⁶ The Ca II lines used to construct the Boltzmann plots are listed in Table 2. A rapid decay in temperature with time from an initial value of 11 000 K at 100 ns after the laser pulse to 7000 K at 10 µs delay time was found. Fig. 7 shows the electron density *versus* the temperature for the different delay times, marked with numbers ranging from 1 for $t_{delay} = 100$ ns to 10 for $t_{delay} = 25$ µs. The trajectory of the plasma state shows the existence of a temperature range running from 7000 K to 10 000 K where only a moderate change—if any—of the electron density occurs. For T > 10 000 K the electron density rises rapidly approaching 3.2×10^{17} cm⁻³ at 11 000 K.

Table 1 Atomic and ionic line parameters²³ and observed line emission decay times

atom or ion	Wavelength/nm	$E_{\rm i}/{\rm eV}$	$E_{\rm k}/{\rm eV}$	decay-1 period/µs	$\tau_1/\mu s$	decay-2 period/µs	$\tau_2/\mu s$
Ar I	706.722	11.55	13.30	0.1–20	2.5		
Ar I	420.067	11.55	14.50	0.1–15	2.4		
Ar I	415.859	11.55	14.53	0.1–25	3.1		
Ar II	434.806	16.64	19.49	0.1–25	2.5		
Ca I	422.673	0	2.93	0.1–3	1.6	4-25	12.7
Ca II	396.847	0	3.12	0.1–5	1.9	10-25	11.3
Ca II	393.366	0	3.15	0.1–5	1.8	10-25	10.7
Ca II	317.933	3.15	7.05	0.1–10	1.5		



Fig. 6 Electron density as a function of the delay time after the laser pulse.

 Table 2
 Ca II lines and parameters²³ used to construct Boltzmann plots

λ/nm	$log\;(g_if_{ki})$	E _i /eV	E _k /eV	
315.887	0.27	3.12335	7.04717	
317.933	0.52	3.15098	7.04955	
370.603	-0.44	3.12335	6.46788	
373.690	-0.15	3.15098	6.46788	
393.399	0.135	0	3.15098	
396.847	-0.18	0	3.12335	



Fig. 7 Electron density as a function of electron temperature. The numbers mark the delay time after the laser pulse, starting from No. 1 for 100 ns delay time and ending at No. 10 for 25 μ s after the laser pulse corresponding to the 10 data points of Fig. 6.

For argon atomic and ionic lines it was not possible to determine an electron temperature using the Boltzmann plot method. The observed atomic lines have upper energy levels very close to each other (between 13 eV and 14 eV) and the ionic argon lines suffer from poor signal-to-noise-ratio being lower than 2. Hence, a reliable temperature determination was not possible in both cases.

Calibration curve

The emission response to varying concentrations of Na within the salt solution was investigated; the obtained calibration curve is shown in Fig. 8.

The laser energy was 110 mJ in this case and the plasma emission was observed using the Echelle spectrometer. Spectra were recorded using a delay time of 800 ns and an integration time gate of 20 μ s. A series of 100 (10 \times 10 pulses) spectra were recorded and averaged. Error bars are equal to the standard deviation of the 10-pulse averages. The fit curve of the double-logarithmic plot shows a linear behaviour with a slope of 0.9 up to a concentration of Na of 0.2 m-%. Beyond this concentration the slope of the curve decreases to 0.5.

There are two possible explanations for this behaviour. On the one hand it can be explained by the concept of the curve-ofgrowth (COG). According to Gornushkin *et al.*,²⁷ who applied the COG method to laser-induced breakdown spectroscopy, non-linearity in the calibration function of solid samples for concentrations in the range between 0.1 m-% and 1 m-% is observed depending on the delay time and the laser energy used. The double logarithmic plot of the theoretical curve of growth has an asymptote with slope 1 for concentrations up to 0.1 m-%, and another with slope 0.5 for higher values. The intersection between these asymptotes marks the point of transition between low and high optical density of the plasma. Because the conditions differ from ours no quantitative comparison can be made here. Gornushkin *et al.* studied the curves of growth of Cr in a steel matrix for solid samples.

The emission of the two Na lines, *i.e.* Na I 589.592 nm and Na I 588.995 nm was tested for self-absorption. Saturation effects can be observed above a concentration of 0.1 m-% supported by the line intensity ratio of these two lines, but the accuracy of the data is not high enough for quantification. For the Na I 589.592 line, which is expected to show a weaker self-absorption, a slope of 0.7 was estimated for concentrations ≥ 0.2 m-%.



Fig. 8 Double-logarithmic calibration curve for particles of all size classes obtained from sodium solution using N_2 as a carrier gas without co-flow. Error bars are multiplied by a factor of 10 for concentrations \geq 0.05 m-%.

On the other hand, the observed behaviour (Fig. 8) could be due to growing particle size with increasing concentration of the solution. The increase of the concentration results in the growth of the size of solid particles remaining when the liquid droplets dry out, which leads to a rise in the total mass concentration of the aerosol. Thus, on the one hand, the reduced increase of the signal above a concentration of 0.2 m-% can be due to incomplete dissociation of larger particles or, on the other hand, due to stronger losses of the larger particles during the transport to the measurement chamber.

However, both effects, *i.e.* plasma properties and particle size effects may play a role here. To investigate the influence of the argon co-flow on the LIBS signal, the signal response to a variation of sodium and calcium with and without the use of the coflow was measured. In this experiment, solutions of sodium and calcium chloride with a elemental mass concentration of 1 m-% each were generated. For the LIBS measurements the solutions were mixed such that the content of Na was successively increased and an aerosol stream was generated as described before. Spectra were recorded with the Echelle spectrometer integrated with a delay time of 800 ns after the laser pulse and a gate width of about 30 µs. The laser energy was 200 mJ and a series of 200 (10 \times 20 pulses) spectra were averaged. The measurements were undertaken with and without an additional argon co-flow. In Fig. 9 the obtained line intensity ratio of Na and Ca for both measurements is plotted versus the mixing ratio of Na and Ca cations of the solution. Fig. 9 shows that the variation of the mixing ratio is well represented by the LIBS signal. The elemental mixing ratio can be clearly derived from the ratio of the measured line intensities. The measurement with an argon co-flow reduces the ratio of the line intensities by an offset. This can be explained by different plasma conditions and excitation conditions for the lines. Because of the enhanced plasma confinement for the argon co-flow, the degree of ionization is expected to increase, which causes a reduced Na I to Ca II signal ratio. By approximating a polynomial function to the data points, the standard deviation of procedure was estimated to be 0.16 for the measurement without argon according to DIN $38402-51.^{28}$ In case of the argon co-flow this value is reduced to 0.032.

Size-resolved measurements

Size-resolved LIBS analysis of calcium particles were undertaken for different measurement conditions and compared to the aerosol size distribution and the particle mass concentration for each size class.

To provide a size-resolved analysis of particle composition, particles generated from CaCl₂ solution as described above were fractionated by size using the DMA. The CaCl₂ solution had a calcium elemental mass concentration of 0.23 m-%. The particle size was scanned from 19 nm up to 800 nm in 27 logarithmic steps, and the fractionated particles were subsequently analysed by LIBS for each size class. The characteristic of the obtained emission line intensity for Ca II at 393.366 nm with increasing particle size is shown in Fig. 1 together with the particle size distribution, which has been discussed in section 'Aerosol sampling'. The plasma emission was observed using the Echelle spectrometer as described above and the laser pulse energy was set to 200 mJ.

Fig. 1 allows a comparison of the line intensity of Ca with the particle size distribution. The Ca line emission intensity follows the particle mass distribution and attains a maximum in the particle diameter range between 350 nm and 450 nm as the mass distribution does.

In Fig. 10 the Ca line intensity is plotted as a function of the particle mass-concentration. Here, a correlation between the particle mass concentration and the obtained LIBS signal can clearly be seen. For small particles the line intensity increases nearly linearly with mass up to a particle diameter of approximately 140 nm (No. 15) and a corresponding mass concentration of 4.5%. From a particle mass concentration of 6% upwards, corresponding to a particle diameter of 220 nm (No. 18) the signal rises more slowly and not as linearly as below. The offset of measurement point No. 18 is due to the two different measurement modes of the CPC. A possible reason for the slower



Fig. 9 Line intensity ratio as a function of the mass concentration ratio of sodium and calcium within the solution. Error bars are multiplied by a factor of 5.



Fig. 10 Line intensity of Ca II 393.366 nm as a function of sizedependent particle mass concentration. Particle diameters are represented by numbers in ascending order as in Fig. 1. All error bars are multiplied by a factor of 10.



Fig. 11 Size-resolved LIBS signal of Ca particles with and without the use of an argon co-flow, measured with the Paschen-Runge spectrometer.

increase may be the influence of the particle size in the laserinduced plasma. Laser-particle interaction of larger particles is different from that of smaller particles. In this regard one aspect could be a different location within the plasma.¹⁹ Furthermore, the interpretation given for the Na calibration curve (Fig. 8) may also be applied here, *i.e.* the particle size.

Fig. 11 shows the line intensity of calcium Ca II 396.847 nm as a function of particle diameter with and without the use of a co-flow. The LIBS signal is analysed by the Paschen-Runge spectrometer with a delay time of 2 μ s and an integration time gate of 25 μ s. The laser energy was 265 mJ in this case and 1000 consecutive single spectra were accumulated. By the use of the Ar co-flow, the LIBS signal is enhanced by a factor of about 1.5. The use of the Ar co-flow does not influence the characteristic of the size-dependent curve significantly.

Conclusions

The development of a LIBS-based measurement system for online, size-resolved analysis of particulate matter was presented. Basic investigations on the system behaviour were undertaken. In this regard the temporal resolution of the system was analysed. It was found that by the use of an additional co-flow signal recovery of the system can be reduced by a factor of 4.5. A short response time and a high temporal resolution to changes in the particle composition is an important fact and show the suitability of the system for the on-line analysis of paticulate matter. To calibrate the measurement system different strategies were tested. In this regard investigations concerning the signal response to total and relative elemental concentration and the particle mass concentration were carried out. The signal response has a similar behaviour as described by the curves-of-growth theory. Electron density and temperature were determined to describe the temporal evolution of the plasma state. Only a moderate change of electron density with temperature was found for a temperature change between 7000 K and 10 000 K, whereas the electron density increases rapidly for temperatures above 10 000 K. Sizeresolved measurements of particles in the size-range between

20 nm and 800 nm were undertaken. Thereby, it was demonstrated that the LIBS signal obtained follows the particle mass distribution.

We demonstrated the suitability of our measurement system for the on-line analysis of particulate matter in a gas stream. By scanning the particle size, size-resolved analysis of particle composition is provided. Different calibration concepts can be realised when particle size as well as particle mass concentration are considered. In the further course of research, investigations will be carried out concerning single particle detection.

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