

High-concentration measurements with optical aerosol spectrometers by signal fluctuation analysis

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ABSTRACT

Optical aerosol measurement systems can be classified into single-particle counting techniques and ensemble techniques. In single-particle counting instruments, such as optical aerosol spectrometers, each particle is analyzed individually. This allows for the accurate measurement of the number concentration and the size distribution of the measured aerosol. Current aerosol spectrometers suffer from a limited concentration range due to coincidence errors. In contrast, ensemble techniques, such as photometers, are suitable for high-concentration measurements. One major drawback of such instruments is that they only provide information about one aerosol property, which is typically the mass concentration. A new ensemble technique for the simultaneous measurement of two aerosol properties, namely particle size and concentration, was developed and experimentally verified. The results show that the median particle size (D_{50}) of a monodisperse aerosol can be determined with a deviation of about 10 %, and the concentration with a deviation of about 30 %. With individual instrument calibration, the accuracy can be further improved to approximately 5 % with respect to particle size and 10 % with respect to concentration. The method may be either implemented as a standalone measurement device or, as an add-on for e. g. optical particle spectrometers in the form of a high-concentration mode.

1. Introduction

Optical aerosol spectrometers are widely used single-particle measuring instruments for the in-situ characterization of a wide variety of aerosols. Particle sizes between 70 nm and 25 μm can be measured (VDI 3867 Blatt 4:2011–16, 2011). The method is based on the evaluation of scattered light. Fig. 1 shows a schematic of the measuring principle. The aerosol is passed through an illuminated measuring volume. If a particle is inside the measuring volume, it scatters light depending on its geometrical and optical properties. For basic geometries, such as spherical particles, the correlation between incident and scattered light can be analytically described by the Mie theory (Mie, 1908). A photodetector converts the light intensity, scattered from each individual particle, to an electrical pulse. The pulses can then be counted and assigned into different classes depending on their amplitude. Each class corresponds to a certain particle size, which is defined by a device-specific calibration curve (VDI 3867 Blatt 4:2011–16, 2011). The result is the number-based size distribution of the measured aerosol. Furthermore, the number concentration of the aerosol can be calculated if the sampling time and sample flow are known. In recent years there have been several approaches to obtain additional information with optical aerosol

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spectrometers. Complex measurement setups with multiple light sources or multiple photodetectors like the dual-wavelength optical particle spectrometer (DWOPS) described in (Nagy, Czitrovsky, Kerekes, Veres, & Szymanski, 2017) enable the determination of material properties like the refractive index of the particles. In (Pitz, Hellmann, Ripperger, & Antonyuk, 2018) a setup for the measurement of the particle sphericity and fractal dimension is proposed.

Due to the coincidence error, the use of each optical aerosol spectrometer is limited to low concentrations (typ. below 10^5 cm^{-3} (VDI 3867 Blatt 4:2011–16, 2011)). Since the measuring volume cannot be infinitely small, the probability of two or more particles inside the measuring volume at a time increases with concentration. As a result, the pulses of the individual particles overlap each other. Such coincidences cause a reduced counting efficiency and shift the size distribution towards larger particles. Until a certain degree, the coincidence error can be minimized by advanced signal processing algorithms (Oeser, Samala, Hillemann, Rudolph, & Lienig, 2022) and coincidence correction techniques (Oeser et al., 2023), (Raasch & Umhauer, 1984, p. 95). If the concentration increases further, there are practically always particles in the measuring volume. Conventional peak detection, i.e., counting the single particle pulses, is no longer possible (cf. Fig. 2). Instead, an integrated signal value has to be evaluated. This mode of operation is similar to the principle of a photometer, where the average value of the detector signal is used to determine the mass concentration of the measured aerosol (Aerosol measurement, 2011).

Photometers can be implemented either in a scattering or extinction-based setup. Based on the Beer-Lambert law Wessely developed a technique for extinction-based photometers that allows the simultaneous measurement of two independent aerosol properties, which are particle size and number concentration (Wessely, 1999). Wessely used the mean value and standard deviation of the detector signal to calculate the size and concentration of an aerosol. This method is nowadays commercialized (PAM 510, Topas GmbH, Germany) and well suited for process monitoring of monodisperse aerosols, especially at high concentrations (Topas GmbH). It was also shown that the statistical fluctuation analysis is well suited for inline monitoring of process sprays. According to the work of Dannigkeit the diameter of monodisperse latex particles can be measured with an accuracy better than 5 %, while the volume concentration can be determined with an uncertainty of less than 12 % (Dannigkeit, Steinke, & Ripperger, 2010). Even for the measurement of the mean droplet size of polydisperse sprays, the statistical fluctuation analysis can achieve an accuracy of better than 5 %. For high concentrations, i.e. if the light transmission through the measuring system is low, the measuring uncertainty is increased, since certain parasitic effects like multiple scattering become more dominant. Schwarz suggested the use of a spatial frequency filter to overcome this issue (Schwarz, Ripperger, & Antonyuk, 2018). Recently, an extinction-based method for the simultaneous measurement of concentration and mean particle size in fluids was developed (Weirich & Antonyuk, 2023). In contrast to the statistical fluctuation analysis, the extinction ratio of multiple wavelengths was used to obtain the additional size information.

In extinction-based measurement setups, the Beer-Lambert law provides a well-known deterministic relationship between the aerosol and the detector signal. Optical aerosol spectrometers commonly use a scattering setup. Here, in contrast to extinction

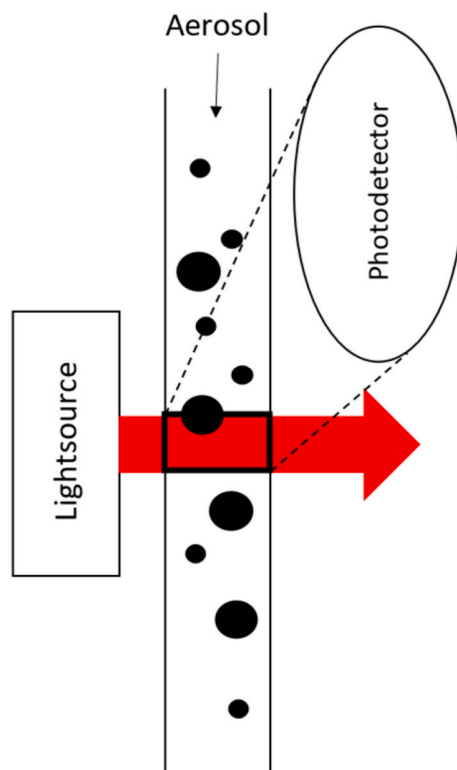


Fig. 1. Basic measurement setup of an optical aerosol spectrometer.

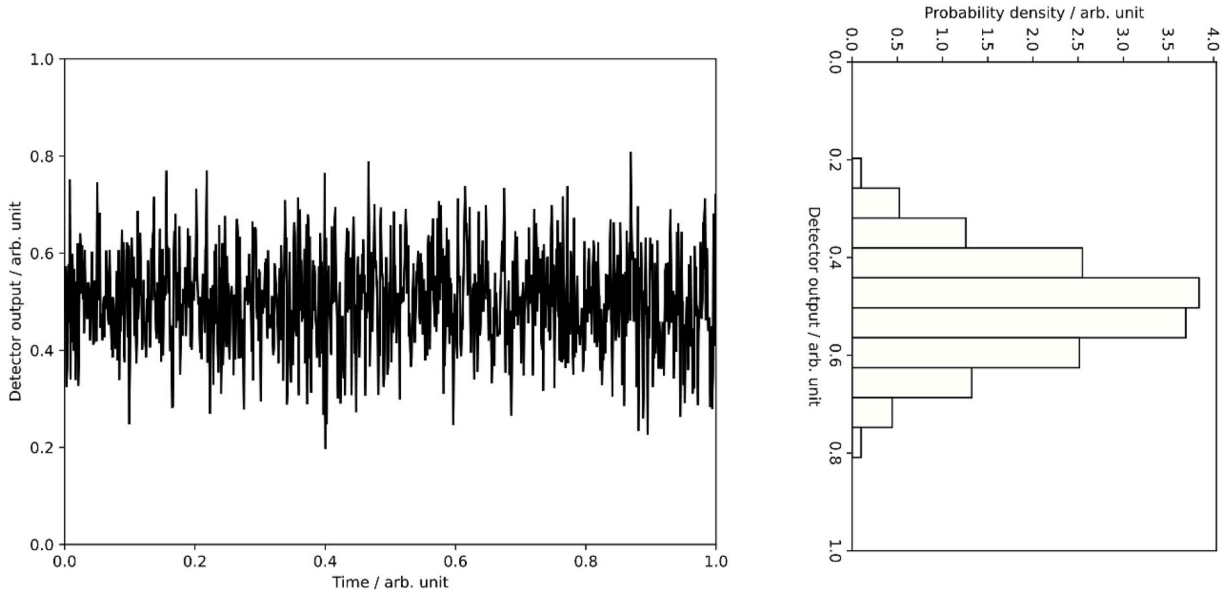


Fig. 2. Principle of fluctuation analysis. Particle size and concentration can be estimated from the shape of the probability density function of the detector signal.

arrangements, the detector signal does not result from the turbidity of the aerosol, but from the sum of the light scattered by each individual particle in the measuring volume. Hence, the fluctuation method of Wessely cannot be used as a high-concentration mode for optical aerosol spectrometers. There have been approaches to finding a relationship between the probability density function of scattered light intensities and the corresponding aerosol. In (Jani et al., 2002) it was found that the probability density function of scattered light intensities is Gaussian-shaped and therefore quite similar to the probability density function of an extinction setup. It was shown that both parameters, particle size and number concentration have an influence on the mean value and standard deviation of the detector signal. However, this relationship has not been used for the measurement of aerosol properties yet.

2. Material and methods

2.1. Fluctuation analysis of optical signals

The simultaneous determination of two independent aerosol parameters (i.e., median particle size and concentration) requires at least two measured parameters. In the proposed method, the additional information is contained in the fluctuations of the scattering signal. Fig. 2 shows a typical detector signal of an optical aerosol spectrometer for the case that the concentration is significantly higher than the coincidence limit of the device. It can be seen that the detector signal contains plenty of fluctuations. Even if those fluctuations look like noise, they are caused by single particles passing the measuring volume and thus contain information about the aerosol. The detection system of common photometers usually has a low bandwidth to remove the fluctuations, since they are unwanted in this application. The calculation of the mass concentration is therefore based on the average signal value. In contrast, the proposed measurement method requires fluctuations. The bandwidth of the detector signal, as well as the sampling rate, have to be fast enough to record the fluctuations of a single particle. The observed signal samples are assigned into different amplitude classes as shown on the right side of Fig. 2. The histogram contains information about the probability density function of the detector signal, which allows the simultaneous quantification of median particle size and concentration. The relationship between the histogram shape and the searched parameters is achieved by fitting a normal or log-normal distribution. Median particle size and concentration are then calculated from the mean and standard deviation of the distribution with a polynomial function.

For basic considerations, it is assumed that the scattering signal of multiple particles inside the measuring volume of an optical aerosol spectrometer is equal to the sum of the scattering signal of each individual particle. Parasitic effects like multiple scattering are neglected in the following simplified model. This assumption is valid as long as the distances between the particles are more than three times their diameter (Kerker, 1969), and the measuring volume is small enough that the attenuation of scattered light due to other particles is negligible. Furthermore, an ideal monodisperse aerosol is assumed, in which each particle causes an equally high pulse amplitude independent of the position inside the measuring volume. It should be noted here that in real optical arrangements, the pulse amplitudes even for exactly similar particles can vary, since measuring volumes practically does not provide an ideal uniform light intensity distribution. The detector Signal U is then given by Equation (1):

$$U(N) = N \cdot U_0 \quad (1)$$

Here N denotes the number of particles, inside the measuring volume at a certain time. U_0 denotes the amplitude of a single particle pulse. The mean value of the detector signal μ_U can be calculated from the mean value of the particles inside the measuring volume \bar{N} as shown in Equation (2):

$$\mu_U = \bar{N} \cdot U_0 \quad (2)$$

The probability for a certain number of particles in the measuring volume at a given time can be described by Poisson statistics. For high concentrations, e. g. if the average particle count in the measuring volume is above 20, the Poisson distribution can be approximated with a normal distribution. The standard deviation of the number of particles inside the measuring volume SD_N is then given by the average number of particles inside the measuring volume (Equation (3)).

$$SD_N = \sqrt{\bar{N}} \quad (3)$$

With the known standard deviation of the particle count in the measuring volume, the standard deviation of the detector signal σ_U can be calculated by Equation (4).

$$2 \cdot \sigma_U = U(\bar{N} + SD_N) - U(\bar{N} - SD_N) = U(\bar{N} + \sqrt{\bar{N}}) - U(\bar{N} - \sqrt{\bar{N}}) \quad (4)$$

After inserting Equation (1), Equation (4) can be rearranged as Equation (5).

$$\sigma_U = \sqrt{\bar{N}} \cdot U_0 \quad (5)$$

Finally, Equation (2) and Equation (5) can be inserted into each other, and be solved for the average number of particles in the measuring volume \bar{N} , as well as the amplitude of a single particle pulse U_0 as shown in Equation (6) and Equation (7).

$$\bar{N} = \frac{\mu_U^2}{\sigma_U^2} \quad (6)$$

$$U_0 = \frac{\mu_U}{\sigma_U} \quad (7)$$

The aerosol concentration can be calculated with the average number of particles in the measuring volume. The particle size is determined from the amplitude of an individual particle signal, using the instrument-specific calibration function which is known from the single particle counting mode. As can be seen, both values can be theoretically calculated from the mean and standard deviation of the detector signal. This allows the simultaneous measurement of size and concentration with a light-scattering photometer.

2.2. Simulation

Although the simplified model contains the general relationship between the detector signal and particle size or concentration, in practice, one will notice significant differences. The Poisson distribution is asymmetric for small expected values. Especially optical aerosol spectrometers are usually designed in such a way that the measuring volume is as small as possible (typically a range of 0.001

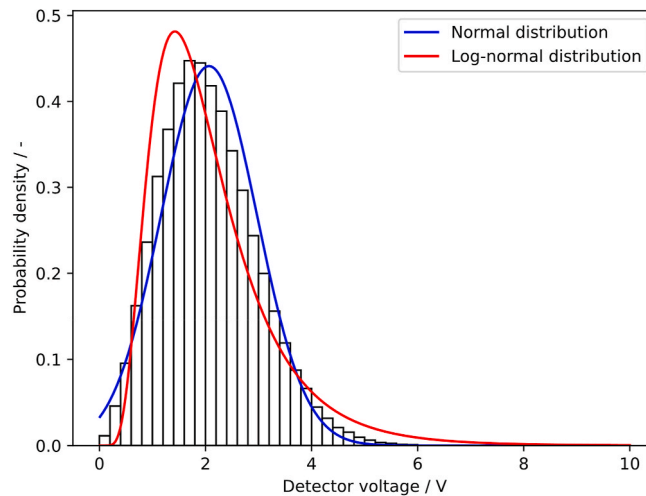


Fig. 3. Simulated probability density distribution of the detector signal. The concentration is $200,000 \text{ cm}^{-3}$. A cylindrical measurement volume with a diameter of 1 mm was considered. The height is given by a Gaussian laser beam with a width of $30 \mu\text{m}$. The size of the individual particles was assumed to be such that the amplitude of a single pulse is 1 V.

$\text{mm}^3\text{--}0.02 \text{mm}^3$), since the coincidence error, and thus the maximum measurable aerosol concentration is directly coupled to it (VDI 3867 Blatt 4:2011–16, 2011). Due to the small measuring volume, the average number of particles in the measuring volume is small. Even for concentrations in the range of one or two orders of magnitude above the device-specific coincidence limit. Therefore, the assumption of a normally distributed detector signal amplitude is questionable. Most commonly, the light intensity inside the measuring volume of a light scattering detector is rather Gaussian distributed than homogeneous. This causes Gaussian-shaped particle pulses (Oeser et al., 2022). Accordingly, the resulting pulse amplitude of two overlapping particle pulses is not the same in any case, but depends on the individual position of the particles inside the measuring volume. This affects also the shape of the distribution of the detector signal. Thus, it is difficult to find a valid analytical relationship between the detector signal and the aerosol parameters of interest.

An alternative approach would be a simulation of the setup. Therefore, a simulation volume is defined, which is significantly larger than the actual measurement volume and completely encloses it. From the product of the measuring volume and the concentration to be considered, it is now calculated how many particles are taken into account for the simulation. Each particle is then randomly distributed inside the simulation volume. For all particles inside the measurement volume, the corresponding detector response is calculated. Depending on the amplitude, the simulation step is assigned to a specific histogram class. If this process is repeated multiple times, the corresponding probability distribution of the detector signal is obtained.

Fig. 3 shows the result of such a simulation for an ideal monodisperse aerosol. In this example, the concentration was chosen, and the average number of particles in the measuring volume was $\mu_N = 4.7$. This value is much higher than the coincidence limit of the device (commonly, $\mu_N = 0.1$ is considered as coincidence limit, refer to (VDI 3867 Blatt 4:2011–16, 2011)). The simulated probability function was approximated as a normal (blue curve), or log-normal (red curve) distribution. As can be seen, the actual distribution neither follows a normal nor a log-normal distribution. However, the simulation model deviates from the theoretical assumptions made in section 2.1, but it can be shown that the detector signal, or at least its probability distribution, contains information about the particle size, and the concentration of the aerosol. The transfer function is a complex relationship, which depends on the specific design of the measuring cell. The simplified model from Equation (6) and Equation (7) is insufficient and will therefore not be used in this work. Since this correlation cannot be solved analytically, the goal of the fluctuation analysis was to find a suitable regression function between the probability distribution of the detector signal and the desired aerosol parameters. Although a regression can be done with different techniques, polynomial regression is used in this work. The procedure of polynomial regression will be explained later in section 3.2.

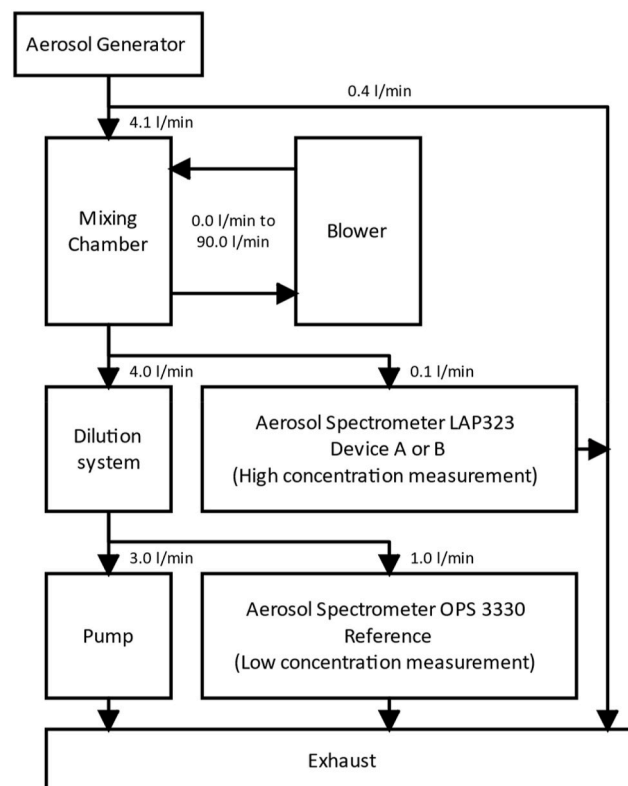


Fig. 4. Measurement setup for data acquisition for fluctuation analysis.

2.3. Experimental setup

The proposed fluctuation analysis requires a regression model, that maps the probability distribution of the detector signal to the parameters median particle size and number concentration of the aerosol. Therefore, an adequate dataset is needed, which contains different data points of a monodisperse aerosol. Each data point must consist of at least the probability density distribution of the detector signal, the median particle size, and the concentration of the aerosol. This requires an aerosol whose particle size and concentration can be varied over a wide range. The concentration must be above the coincidence limit of the device used for the evaluation. In this work, a commercially available optical aerosol spectrometer was used. The basic idea for the reference measurement is to dilute the original aerosol by a fixed factor so that a second optical aerosol spectrometer can be used. If the dilution factor is known, the reference device can not only determine the median particle size but also the number concentration of the original aerosol. Fig. 4 shows the experimental setup used in this work.

The monodisperse test aerosol is generated by a Sinclair-La Mer generator (SLG 270, Topas GmbH, Germany (Sinclair & La Mer, 1949)). The generator consists of a Collison-type aerosol generator (May 1973), which generates small primary particles from a NaCl solution. The particles are passed through the integrated diffusion dryer unit to reduce moisture for the formation of solid salt crystals. A working fluid is evaporated at high temperatures and mixed with primary particles. In this work, Di-Ethyl-Hexyl-Sebacat (DEHS) was used, since this material has a low vapor pressure and thus a high evaporation time. Hence, the change of the particle size over analysis time is neglectable. Further, DEHS generates charge-neutral spherical particles with quasi unit density (i.e., density of 1 g/cm³). The mixture is cooled down in a condensation chimney. The primary particles act as condensation nuclei on which the evaporated working fluid condenses. This heterogeneous condensation process defines the particle size, which can be adjusted by the saturator temperature. Nitrogen was used to operate the generator to avoid fire ignites.

Although the number concentration of the test aerosol can be adjusted by the number of primary particles in the generator, this approach has some disadvantages. The concentration of primary particles has a direct influence on the particle size. So it would not be possible to change the aerosol concentration independently. Therefore, the concentration is adjusted with a variable dilution. In this work, a mixing chamber was used in combination with a controlled blower (RFU 564, Topas GmbH, Germany) which operates in a closed loop. In this configuration, the number concentration of the test aerosol can be varied over a wide working range. Although the blower used in this work provides an internal HEPA filter for cleaning the circulating air, it is recommended to add an additional external filter to avoid contamination due to the high mass concentration.

An optical aerosol spectrometer (modified LAP 323, Topas GmbH, Germany) was used to evaluate the principle of scattered light fluctuation analysis. The total sample flow rate of the device, which is 3.0 l/min, is internally divided into a bypass flow (2.9 l/min) and the actual sample flow (0.1 l/min) through the measuring volume. To prevent DEHS contamination of the device in the bypass stream, only the actual sample flow was used. Due to the significantly reduced flow, care must be taken to make the sampling aerosol path as short as possible. The detector signal of the modified spectrometer was captured using a Field Programmable Gate Array (FPGA) prototyping platform (Eclipse Z7, Digilent, USA) in combination with an analog-to-digital converter (ADC) module (Zmod Scope 1410–125, Digilent, USA). Each measured amplitude was assigned to one of a total of 1024 equidistant classes in the Voltage range from 0 V to 10 V. The result of this measurement is the probability distribution of the detector output voltage.

The precise measurement of the median particle size and the concentration of the test aerosol requires a high dilution. For this purpose, two controlled static dilution systems (DIL 550, Topas GmbH, Germany) were used. Downstream of the dilution stage, the reference measurement was done with an optical aerosol spectrometer (OPS 3330, TSI, USA). To keep the settling time of the aerosol at the measuring instruments as short as possible, a pump was used in parallel to the reference instrument, so that the total flow through the dilution stage is 4.0 l/min. Note that the dilution systems used in this work can be calibrated to achieve a certain dilution rate for a specific flow. The exact dilution factor does not influence the result of our measurement, as long as it is large enough to prevent coincidence errors in the downstream spectrometer, and small enough to achieve statistically reliable results. The actual dilution factor of the setup was determined with PSL particles at a lower concentration, so that the upstream spectrometer could also be used in single particle counting mode with negligible coincidence error. The dilution factor of the experimental setup was approximately 1:16,000. The number concentration measured by the reference spectrometer has to be multiplied by this factor to get the actual number concentration of the test aerosol.

Care must be taken to install the experimental setup vertically, in order to minimize sedimentation losses for larger particles (>1 μm). The concentration of the test aerosol can be adjusted by the flow of the controlled blower, while the particle size is adjusted by the saturator temperature of the aerosol generator. Especially if the acquisition of the dataset is automated, it makes sense to change the flow of the dilution stage between every measurement point, and the saturator temperature of the aerosol generator only after each measurement series, since the step response of the experimental setup is much faster for changes in the flow of the controlled blower, compared to changes of the saturator temperature. In this work, a sampling time of 30 s was used for each data point. After each measurement, the flow through the mixing chamber or the saturator temperature was changed. A lead time of 30 s was used before the following measurement. After a variation of the saturator temperature, the data acquisition was suspended until the desired temperature was reached. The recorded probability function of the upstream spectrometer, as well as the measurement result of the downstream reference spectrometer were saved for each data point.

3. Results and discussion

3.1. Data acquisition

Fig. 5 shows selected particle size distributions from the generated dynamic test aerosol as measured by the reference spectrometer. As can be seen, the particle size can be adjusted over a wide range by the saturator temperature. Due to the limited size resolution of the operated reference spectrometer, the geometric standard deviation was rated at about 1.2 slightly worse than it actually was.

Within this work, two datasets were recorded. Each of the datasets was recorded with a different aerosol spectrometer of the same type (in the following device A and device B). This will allow some general assumptions about how individual device tolerances influence the measurement result and whether a device-specific calibration is strictly necessary for the fluctuation analysis. Fig. 6 shows the dataset of device A. The concentration varies in a range between $100,000 \text{ cm}^{-3}$ and $6,000,000 \text{ cm}^{-3}$. The median particle size of the data points varies in a range from $0.3 \text{ }\mu\text{m}$ to $2 \text{ }\mu\text{m}$.

Fig. 6 shows that the concentration and particle size of the dynamic test aerosol were adjusted independently of each other with the proposed setup. Note that the data points are located within two approximately rectangular-shaped areas ($0.3 \text{ }\mu\text{m}$ – $0.5 \text{ }\mu\text{m}$, $400,000 \text{ cm}^{-3}$ to $6,000,000 \text{ cm}^{-3}$; $0.5 \text{ }\mu\text{m}$ – $2.3 \text{ }\mu\text{m}$, $100,000 \text{ cm}^{-3}$ to $1,500,000 \text{ cm}^{-3}$). In the area with the coarser particles, the concentration is lower. Here the flow of the controlled blower was operated within a higher range. This was necessary because it was already shown during the recording of the dataset that the detector signal of the measurement setup overdrives at high concentrations and coarse particles. Due to the saturation, which is caused by the electronics of the optical aerosol spectrometer used in this work, the measured signal histogram would not contain a representative amplitude distribution. Note that a measurement instrument, if specifically optimized for fluctuation analysis, could have a much wider dynamic range. This can be achieved by e. g. reducing the laser power or reducing the gain of the photodetector when saturation occurs.

The proposed method is only feasible, as long as the probability distribution of the detector signal shows a proper peak. I. e., the detector signal is neither on the baseline nor in the saturation of the detector signal for most of the time. In this case, the values of the marginal classes of the histogram would dominate. This requirement limits the range of applications for the fluctuation analysis with respect to number concentration. Invalid probability distributions are relatively easy to determine. All data points where the maximum of the probability distribution is smaller than the values of the marginal classes are discarded (Refer to Fig. 7). The remaining data points are highlighted in red in Fig. 6. For the following evaluation, only the “valid” data points are used. Note that the lower detection limit with respect to particle size depends on the optical design of the measuring cell. According to the datasheet of the aerosol spectrometer used in this work, the lower detection limit is about 150 nm . It is to be expected that the lower detection limit with respect to particle size is even smaller for high concentrations, since the particle pulses overlap each other, which increases the total amplitude. However, the aerosol spectrometer used for the reference measurement has a lower detection limit of 300 nm .

The final dataset is used for a polynomial regression. The sampled histograms consist of 1024 different amplitude classes. A regression model with 1024 input variables would be very complex, and more likely to be unstable. Thus, the histogram data has to be compressed. The challenge is to describe all of the 1024 variables, with as few variables as possible, without losing significant information about the median particle size and the number concentration of the aerosol. This can be achieved by describing the histogram data with a normal or log-normal distribution. Those distributions depend on only two parameters, namely mean value μ and standard deviation σ , as shown in Equation (8) and Equation (9). The variable U corresponds to the pulse amplitude.

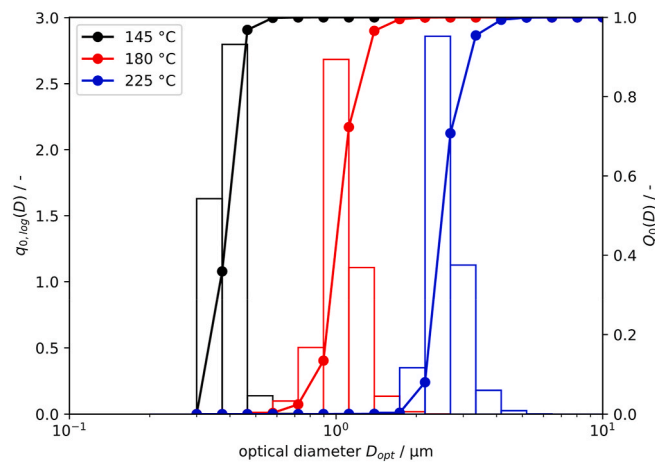


Fig. 5. Reference measurement. Transformed number-weighted size distribution densities ($q_{0,\log}(D)$, histograms) and number-weighted cumulative size distributions ($Q_0(D)$, solid lines) of the monodisperse DEHS test aerosols for different saturator temperatures plotted against optical diameter obtained with the reference spectrometer. Graphical representation according to ISO 9276–1:1998 (ISO 9276–1:1998–06, 1998).

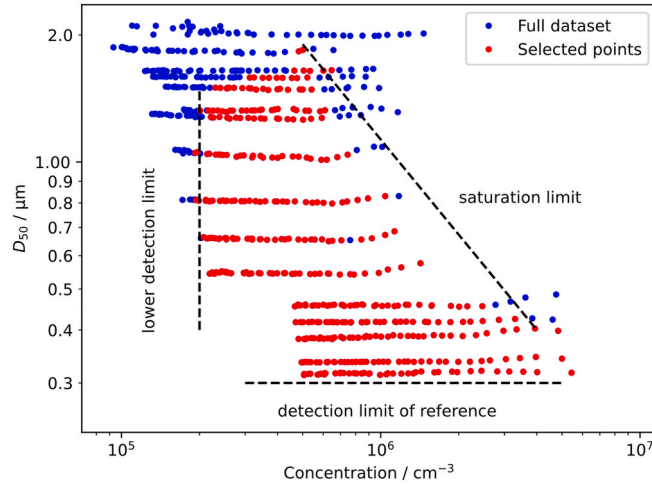


Fig. 6. Dataset of device A. Concentrations and median particle sizes of the test aerosol.

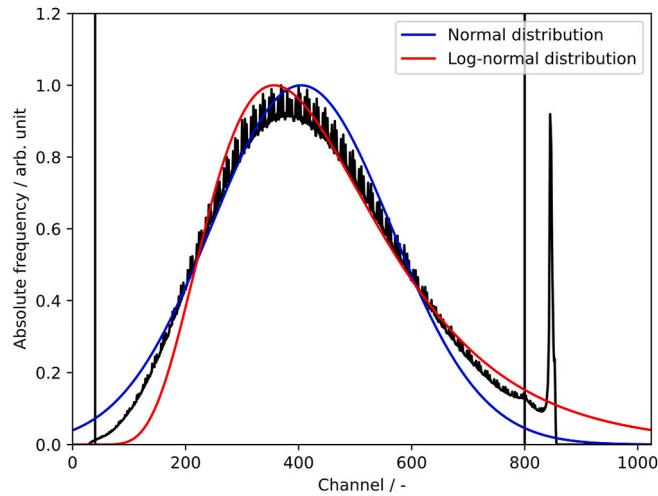


Fig. 7. Probability distribution of the detector signal. The median particle size is $1.49 \mu\text{m}$ and the concentration is $544,908 \text{ cm}^{-3}$ (device A). Fit of a normal and log-normal distribution to the measured histogram. Marginal classes are not considered for the regression.

$$\varphi = \exp\left(-\frac{(U - \mu_{Normal})^2}{2 \cdot \sigma_{Normal}^2}\right) \quad (8)$$

$$\varphi = \exp\left(-\frac{(\ln U - \mu_{Log})^2}{2 \cdot \sigma_{Log}^2}\right) \quad (9)$$

Note that Equation (8) and Equation (9) slightly deviate from the common normal and log-normal distribution models. Usually the probability distributions are normed in such a way that the integral over the whole distribution is equal to one. In this work, the distributions, and the measured histograms are scaled in such a way that the maximum value is one. Otherwise, the distribution shape of the measured histogram would be significantly affected as soon as the detector signal contains amplitudes close to the signal baseline or the saturation limit (cf. Fig. 7). Since the recorded probability distribution might be influenced by either the baseline or the saturation limit of the detector, only the values between the vertical lines were considered for the regression. The determination of the mean value μ and standard deviation σ is a nonlinear optimization problem. Fig. 7 shows the measured probability density for a single data point. The corresponding normal and log-normal distributions are plotted as blue and red curves. As already seen in the simulation (cf. Fig. 3), both models do not exactly match the actual amplitude distribution. This result differs from the distribution shapes reported by Jani where the measured intensities follow a Gaussian distribution (Jani et al., 2002). The differences are caused by the non-uniform light intensity distribution in the measuring volume of the optical aerosol spectrometer. In the work of Jani, a measuring volume of 6.5 cm^3 with a uniform light distribution was evaluated. Further, the average amount of particles inside the measuring

volume was 650, whereas the average amount of particles inside the measuring volume in Fig. 7 was somewhere around 10. For such small numbers, the simplification of the Poisson distribution as a normal distribution is erroneous.

3.2. Polynomial regression

The input data of the regression model only consists of the two variables mean and standard deviation. One of the most popular regression methods is least squares. Although the technique is mostly used for one-dimensional problems, least squares can also be used for multidimensional problems. For two-dimensional problems, as is the case for the fluctuation analysis (e. g. the concentration is calculated from the mean value and standard deviation of the signal amplitude), the result of the regression corresponds to a more or less complex surface, depending on the polynomial degree (cf. Fig. 8). The surface defines an analytical relationship between two independent variables x and y , and an output variable z (Equation (10)). The surface is a model of the observed data points and should approximate them as well as possible. For example, the equation of a surface with a second-order polynomial in x -direction, and a first-order polynomial in y -direction is given by Equation (10).

$$z = f(x, y) = a_0 + a_1 \cdot x + a_2 \cdot x^2 + a_3 \cdot y + a_4 \cdot x \cdot y + a_5 \cdot x^2 \cdot y \quad (10)$$

Assume a series of measured data points, which should be approximated by the surface. For each data point, the distance between the surface and a data point in the z -direction can be written as Equation (11).

$$s_1 = a_0 + a_1 \cdot x_1 + \dots + a_5 \cdot x_1^2 \cdot y_1 - z_1, s_2 = a_0 + a_1 \cdot x_2 + \dots + a_5 \cdot x_2^2 \cdot y_2 - z_2, s_3 = a_0 + a_1 \cdot x_3 + \dots + a_5 \cdot x_3^2 \cdot y_3 - z_3 \dots \quad (11)$$

Or alternatively in matrix notation as shown in Equation (12).

$$S = M \cdot A - Z \quad (12)$$

The Matrix M is then given by Equation (13).

$$M = \begin{pmatrix} 1 & x_1^1 \cdot y_1^0 & x_1^2 \cdot y_1^0 & x_1^0 \cdot y_1^1 & x_1^1 \cdot y_1^1 & x_1^2 \cdot y_1^1 \\ 1 & x_1^0 \cdot y_1^0 & x_1^0 \cdot y_1^0 & x_1^0 \cdot y_1^0 & x_1^0 \cdot y_1^0 & x_1^0 \cdot y_1^0 \\ \dots & \dots & \dots & \dots & \dots & \dots \\ 1 & x_n^0 \cdot y_n^0 & x_n^0 \cdot y_n^0 & x_n^0 \cdot y_n^0 & x_n^0 \cdot y_n^0 & x_n^0 \cdot y_n^0 \end{pmatrix} \quad (13)$$

The quality of the fitted surface can be expressed as the sum of the squared differences between each data point z_i and the surface $f(x_i, y_i)$. The surface is well-fitted when the distance to all measured points is minimal. So the goal of the regression is to minimize the following error term (Equation (14)).

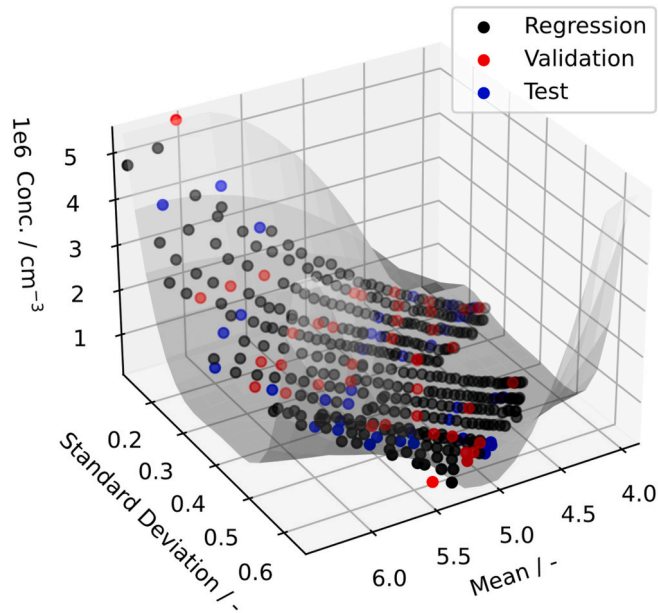


Fig. 8. Concentration against the mean value μ_U and standard deviation σ_U . Data points are used for regression, validation, and testing, as well as the least squares optimized surface. (polynomial degree: 2 in the direction of mean value, and 5 in the direction of standard deviation).

$$\sum s_i^2 = \sum (z_i - f(x_i, y_i))^2 \quad (14)$$

It can be shown that the term is minimal if the polynomial coefficients are calculated according to Equation (15).

$$a = (M^T \cdot M)^{-1} \cdot M^T \cdot Z \quad (15)$$

With this method, surfaces with different complexity can be generated. The polynomial degree selected for the x-direction, and y-direction is responsible for the accuracy of the regression model. If the polynomial degree is chosen too low, complex relationships, such as curvatures in the surface cannot be approximated sufficiently. On the other hand, if the polynomial degree is chosen too high, overfitting may occur. In this case, the model would be poorly regularized. To find a proper choice for the polynomial degree, the dataset was randomly split into three sub-datasets (cf. Fig. 8). The first and largest dataset (80 % of all data points) is only used for the regression itself. A surface was calculated for different combinations of polynomial degrees in the x- and y-direction. The second dataset (10 % of all data points) was then used to find the best-regularized regression surface. The remaining 10 % of the data points were used as test data for the final model. So the evaluation of the fluctuation analysis is only based on data points that have neither been used to calculate the regression function, nor to choose the best surface. With this method, a total of four different surfaces was calculated.

- Number concentration from the normal distribution model
- Median particle size from normal distribution model
- Number concentration from log-normal distribution model
- Median particle size from log-normal distribution model

3.3. Evaluation

In this work, two datasets with roughly the same number of samples were recorded. Each of the datasets was acquired with a different aerosol spectrometer of the same type. The dataset of device A was used for the regression. The dataset of device B was only used for the evaluation of the fluctuation analysis on an uncalibrated device. Note that the evaluation of device A is based on only a minor portion of randomly selected data points (42 data points), since the rest of the dataset was used to fit the regression model. In contrast, the evaluation of device B was done with the complete dataset (469 data points).

To evaluate the fluctuation analysis, the result of the regression models is calculated for each of the known test data points. The result obtained for the median particle size and the concentration is then compared with the result of the reference aerosol spectrometer. For each data point, the relative error can be calculated. As it is not feasible to evaluate every single data point, the result is evaluated statistically. Table 1 shows the mean value and standard deviation of all relative errors. The mean value describes the systematic error, while the standard deviation describes the random error.

Table 1 shows that the systematic error for all regression models of device A is small and can be neglected. The standard deviation, which corresponds to the accuracy of the fluctuation analysis is smaller than 10 %. For the regression model which is based on the log-normal distribution the measurement of the median particle size is even better than 5 %. This result shows that the principle of the fluctuation analysis is well suited for a simultaneous measurement of the number concentration and particle size of a monodisperse aerosol.

The histograms in Fig. 8 show the absolute frequencies of the relative measurement errors on the test dataset from both devices. Since the histograms look quite similar for the normal and log-normal regression models, only the result for the log-normal model is depicted. The result for the test data set of device A is shown in the upper row. Both distributions are centrally located and have no significant systematic deviation. The particle size is calculated with an error smaller than 10 % in almost all cases. Even the calculation of the number concentration has a deviation of less than 10 %, although the distribution appears somewhat broader than for the particle size. This tendency does fit the results of Table 1. Apparently, the median particle size can be estimated with higher accuracy than the number concentration of the aerosol. This is similar to the statistical fluctuation analysis for extinction setups. In (Dannigkeit et al., 2010) an accuracy of 5 % for the measurement of the particle size and an accuracy of 12 % for the measurement of the (volume) concentration of latex particles was achieved.

Due to the manufacturing process of a particle measurement instrument, there may be various deviations from device to device. E.

Table 1

Results of the fluctuation analysis. The mean and standard deviation (SD) of the relative errors were calculated for each data point.

Dataset	Device A				Device B			
	42 (Test data)				469			
Test Size								
Parameter	Size		Concentration		Size		Concentration	
Method	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Poly-Fit (Norm.)	0 %	9 %	0 %	7 %	12 %	58 % ^a	258 %	5170 % ^b
Poly-Fit (Log.)	1 %	4 %	-1 %	10 %	9 %	9 %	-2 %	26 %

^a 5 extreme outliers in the complete dataset. Excluding these 8 % (mean) und 10 % (standard deviation).

^b 6 extreme outliers in the complete dataset. Excluding these -3 % (mean) und 33 % (standard deviation).

g. different dark currents of the photodetector, different offset voltages in the signal chain, or tolerances of the optical components. As a result, the regression function of each individual device is slightly different. For this reason, it is common that particle measurement instruments to be calibrated. E. g. the calibration function of an optical aerosol spectrometer is usually determined with monodisperse PSL particles. For the fluctuation analysis, the individual calibration process would be relatively time-consuming and expensive, since a complete dataset is required. Therefore, the dataset of the second device (device B) is used to estimate whether an individual instrument calibration is mandatory in each case. According to the results of Table 1 and Fig. 9, the measurement result is noticeably worse, if the regression function of device A is used to calculate the measurement results of device B. Especially the calculation of the median particle size, but also the calculation of the number concentration, has a systematic error. This can also be seen in the frequency distributions of Fig. 9. It shows that the measurement of the number concentration is more sensitive to device-specific tolerances than the measurement of the median particle size. The measurement error is almost 30 % for the concentration measurement, and less than 20 % with respect to particle size. This is still feasible for many real-world applications. An individual device calibration may be necessary if a higher accuracy is needed. Note that only two instruments were investigated in this work. The result of two devices may not be representative.

As can be seen in Table 1 the measurement errors of both, number concentration and median particle size, are extremely high for the regression with the normal distribution model on device B. This is caused by several outliers. Without the worst 5 or 6 data points, the errors are within the same range as for the log-normal model. It can be shown that the outliers are systematically located close to the minimum concentration on the fluctuation analysis. The scatter plot in Fig. 10 shows the absolute relative errors for the determination of the number concentration for the complete dataset of device B in dependency of the reference concentration. The

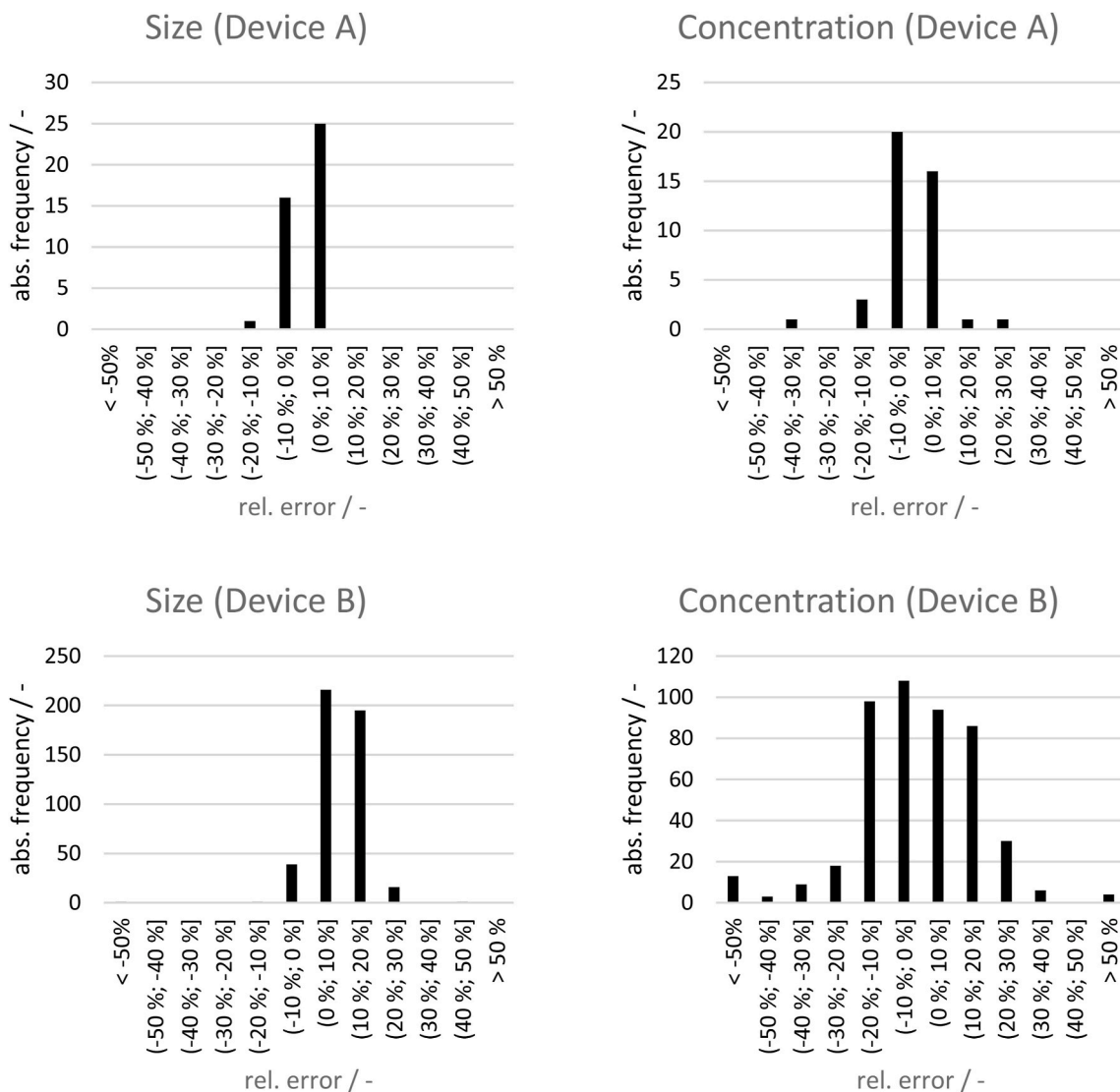


Fig. 9. Frequency distributions of the relative errors of the regression result (log-normal distribution).

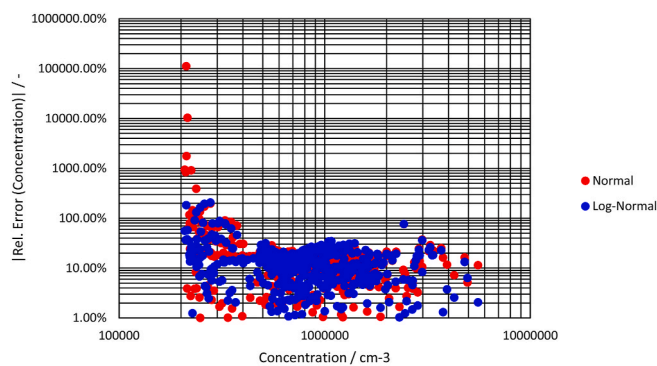


Fig. 10. Absolute relative error of the fluctuation analysis for the calculation of the number concentration on an uncalibrated device (Device B). Datapoints with an error below 1 % are not plotted.

regression results with the normal and log-normal distribution models are compared. Almost any data point has an error below 30 %. For small concentrations, near the lower detection limit of the fluctuation analysis, the errors tend to be higher for both regression models. However, the model which is based on the normal distribution is more sensitive in this concentration range and can give values that deviate several orders of magnitude. Hence, the log-normal regression model should be preferred. In general, care must be taken to only use the fluctuation analysis for aerosols with an adequate number concentration, since the method requires a minimum average amount of particles inside the measuring volume.

3.4. Future work

For the devices used in this work, the minimum number concentration for the fluctuation analysis is estimated to be above 200,000 cm^{-3} , which corresponds to an average amount of particles inside the measuring volume of $C_m \cdot V_m = 2$. In contrast, conventional optical single-particle counting instruments usually have a coincidence limit of $C_m \cdot V_m = 0.1$, which corresponds to the maximum concentration of approximately 10,000 cm^{-3} for the aerosol spectrometers used in this work. If the fluctuation analysis is implemented as an add-on, e. g. a high concentration mode, for such devices, there is a small concentration range, in which neither the single particle analysis, nor the fluctuation analysis is feasible. Advanced signal processing techniques, or a variable measuring volume might be used to close this gap.

4. Conclusion

A new method for the simultaneous measurement of median particle size and number concentration of monodisperse aerosols was proposed. The fluctuation analysis uses statistical signal parameters from the frequency distribution of the detector signal to calculate the units of interest. The method was evaluated with a quasi-monodisperse DEHS test aerosol with a median particle size between 300 nm and 2 μm and a number concentration between 100,000 cm^{-3} and 6,000,000 cm^{-3} . The results show that the median particle size of a monodisperse aerosol can be determined with an accuracy better than 10 % and the number concentration with an accuracy better than 30 %. With individual device calibration, the accuracy can be further improved. The proposed method can be either implemented as a specific measurement instrument or as a high-concentration mode for e. g. optical aerosol spectrometers. In future work, the performance of the method must be evaluated for polydisperse aerosols.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Lukas Oeser, Nakul Samala, Lars Hillemann, Daniel Göhler, Jan Müller, Claudia Jahn-Wolf, and Jens Lienig have no conflict of interest. Lukas Oeser, Nakul Samala, Lars Hillemann, Daniel Göhler, Jan Müller and Claudia Jahn-Wolf are employees of the Topas GmbH, a company that develops, produces and markets aerosol technologies for research and industrial applications.

Data availability

The data that has been used is confidential.

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