From nanoparticles to large aerosols: Ultrafast measurement methods for size and concentration

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Abstract. A major challenge in aerosol technology is the fast measurement of number size distributions with good accuracy and size resolution. The dedicated instruments are frequently based on particle charging and electric detection. Established fast systems, however, still feature a number of shortcomings. We have developed a new instrument that constitutes of a high flow Differential Mobility Analyser (high flow DMA) and a high sensitivity Faraday Cup Electrometer (FCE). The system enables variable flow rates of up to 150 lpm, and the scan time for size distribution can be shortened considerably due to the short residence time of the particles in the DMA. Three different electrodes can be employed in order to cover a large size range. First test results demonstrate that the scan time can be reduced to less than 1 s for small particles, and that the results from the fast scans feature no significant difference to the results from established slow method. The fields of application for the new instrument comprise the precise monitoring of fast processes with nanoparticles, including monitoring of engine exhaust in automotive research.

1. Introduction

Fine and ultrafine particles are commonly classified with a Differential Mobility Analyser (DMA). The classification (i.e. the selection of a well defined fraction from a broad size distribution) occurs in the electrostatic electric field in the annulus between inner and outer electrode of the DMA, where the particles in the sample air drift through the particle free sheath air. Only particles of a certain size reach a narrow slit at the bottom of the inner electrode and thus a downstream detection system. The size distribution of the particles can be measured by a stepwise or stepless change of the DMA voltage. If the DMA voltage is fixed, the DMA acts as particle generator for particles of well defined mobility diameter.

Such conventional DMAs are common and reliable instruments. They feature, however, several shortcomings which limit the field of application:

1. The resolution of particle size, being controlled by the ratio of sheath air flow to sample air flow (at least when this ratio not too high), is limited due to the relatively low sheath air flow rate of typically 3 – 20 lpm. The resolution is typically around 10.

2. The size resolution for very small particles (D < ~20 nm) is additionally deteriorated due to the effect of particle diffusion.

3. The diffusion of particles causes as well high losses of these smallest particles and thus a low sensitivity of the instrument in that size range.

4. The size range of the DMA, being controlled by the sheath air flow rate, features a lower limit of typically 5 nm.
(5) The measurement of size distributions is slow due to the long residence time of the particles in the DMA.

The nearly monodisperse particles downstream of a DMA are frequently detected with a Condensation Particle Counter (CPC). A typical CPC, however, detects only particles larger than ~5 nm and the response time is slow. Thus, a CPC is not the optimal detection system for a high flow DMA system for fast measurements of particles down to the 1 nm size range.

Hence, for the high flow DMA, a Faraday Cup Electrometer (FCE) is used to detect charged particles. Such a FCE features a higher detection limit for particle concentrations than a CPC, but the response time is below 100 ms and there is essentially no lower limit for the detected particle size. Figure 1 illustrates the principle of a FCE. Sample air is drawn through a filter inside the Faraday Cup and the Faraday Cup gains a net charge whenever charged particles enter it. The well isolated Faraday Cup is then discharged with a current passing through a 1 TΩ resistor. This current is converted to a voltage and amplified with a low-noise electrometer. The particles are permanently retained in the Faraday Cup on a filter of high loading capacity.

Minimizing the noise of the electrometer requires a sophisticated geometry with a space between Faraday Cup and outer casing. For the GRIMM FCE, this space is continuously flushed with a rinse air flow in order to achieve the shortest possible response time and to avoid any contamination of the surface of the insulators [1].

![Figure 1. Schematic of the FCE.](image)

2. High flow DMAs

Rosell-Llompart et al. [2] have demonstrated that the shortcomings listed above can be resolved by using a high sheath air flow rate for a short Vienna type DMA. Rosser [3, 4] presented a high flow DMA, which was as well based on the Vienna type design but which featured a considerably reduced exhaust pressure drop. A further improved design was presented by Fernandez de la Mora [5], where a new widely open sheath gas exhaust system produces essentially no pressure drop at all. The main challenge for high flow DMAs is keeping the flow between the electrodes laminar despite of the very high Reynolds numbers. For the later designs, laminar flow was accomplished with an accelerating flow in the working region. Another problem of the high flow DMA is that accurate measurements of the very high sheath air flow rates become very difficult.

The design of the new GRIMM high flow DMA is based on the commercial GRIMM Vienna-type DMAs. Head and bottom of the DMA were however adapted to the much higher sheath air flow rate. To establish a symmetric flow in the annulus between the electrodes, the head of the high flow DMA features a special slit as an inlet for the sample air.

The sheath air is generated by a membrane pump with eight pump heads. Therefore, critical nozzles can be employed to achieve a well defined flow rate of the sheath air. Using two parallel critical nozzles, flow rates of 75 lpm and 150 lpm can be selected. The high flow DMA is operated in the recirculation mode, i.e. the excess air from the end of the DMA is passed through a filter and
reused as sheath air. To prevent a heating of the system by the pumps, two aerosol coolers are employed downstream of the pump. The complete pump module is separated from the DMA in order to have only a minimum of equipment on the table.

Table 1. The size range of the GRIMM high flow DMA.

| DMA type | Active length of electrodes [mm] | Size range at 75 lpm sheath air [nm] | Size range at 150 lpm sheath air [nm] |
|----------|---------------------------------|--------------------------------------|--------------------------------------|
| S-DMA    | 15                              | 0.4 – 19.6                           | 0.3 – 13.8                           |
| M-DMA    | 88                              | 1.1 - 50                              | 0.8 - 34                              |
| L-DMA    | 350                             | 2.1 - 107                             | 1.5 - 72                              |

Three electrodes of different lengths are available, termed S-DMA, M-DMA and L-DMA. The short electrode (S-DMA) features a length of 14 mm, the middle electrode (M-DMA) a length of 88 mm, and the long electrode (L-DMA) a length of 350 mm. The size range of the three DMAs in the high flow mode is shown in Table 1. As shown in Figure 2, the DMA is directly attached to the FCE in order to minimize the particle losses between outlet of the DMA and detection system.

3. Application examples for high flow DMAs

3.1. Characterisation of aerosol standards with nanometer dimensions

Particles of standardized size are very useful in aerosol studies for instrument evaluation and calibration. For particle sizes larger than 100 nm, such standard aerosols are generated by atomizing suspensions of polystyrene latex particles. Below that size range, however, no precise size standards can be generated with this method mainly because the surfactants dissolved in the suspension remains on the surface of the particles. Much smaller size standards are achievable with electrospaying solutions of large organic salts. These organic salts end up in individual ions of the dissolved cation, or in ion clusters with one or more charges. Thus the size range of 1 – 3 nm can be covered. Ude et al. [6] have characterized such size standards using a high flow DMA and the results suggest that the particle mobility diameter can be determined with an accuracy of approximately 1%.
3.2. Fast measurements of size distributions

We have conducted a number of experiments with the main aim of showing that our high flow DMA permits a considerable shortening of the sampling time without significant loss of resolution and sensitivity. To generate the test aerosol, we have adapted the methods described by Ude [6] and we have electrosprayed solutions of Tetra-butyl ammonium iodine (TBAI) and Tetra-pentyl ammonium iodine. Size distributions were measured both with the M-DMA and the S-DMA, sheath air flow rate was 150 lpm and the sample flow rate 5 lpm. No neutralizer was used for these measurements. The sampling time for a single channel was varied from 250 ms to 62.5 ms, the later value corresponds to the sampling frequency of the employed FCE, 1/16 Hz. Figure 3 shows that the shortening of the sampling time from 250 ms to 62.5 ms has no significant effects on the measured size distributions; this is only possible with the fast response time of the GRIMM FCE.

With the 62.5 ms sampling time, the size distributions shown below, representing 62 channels for the M-DMA and 44 channels for the S-DMA, are measured within 3.9 s and 2.8 s. It is obvious that a wider spacing of the measured particles diameters or a reduced size range would enable shorter scan times of well below 1 s. For these measurements the sampling time was limited by the FCE, however, a higher sampling frequency version of the FCE is under construction and with such an instrument the speed of the measurements would be limited only by the residence time of the particles in the DMA. The residence time is, for the sheath air flow rate of 150 lpm, 0.04 s for the S-DMA and 0.25 s for the M-DMA, thus the time for a scan could be decreases to well below 1 s.

Figure 3. Size distributions of ions and clusters measured with the GRIMM high flow DMA. Upper panel: Scan measured with the M-DMA, lower panel: measurement with the S-DMA.
3.3. Generation of monodisperse soot particles for automotive applications
The EURO 5 regulations for Diesel emissions include the measurements of particle number concentrations [7]. The measurements are accomplished with a CPC which has to be calibrated. For calibration, the candidate CPC is operated, as illustrated in Figure 4, in parallel with a FCE that serves as a primary reference. Both counters - candidate CPC and reference FCE – must be supplied with identical concentrations of monodisperse soot particles from a Combustion Aerosol Standard (CAST). Number concentrations measured by the CPC are then evaluated against the concentrations measured by the reference FCE. These calibrations employ normally several instruments downstream of a single DMA, and therefore the sum of the sample flows may easily be as high as several litres per minute. The high total sample flow makes it difficult to achieve monodisperse aerosols of narrow size distribution with a conventional DMA; narrow size distributions can however be achieved if a high flow DMA is employed for the classification.

Figure 4. Setup for the calibration of the CPC using the FCE as a reference.

4. Conclusions and Outlook
Using a conventional Vienna-type DMA with a sheath air flow rate of 150 lpm expands the possibilities of the instrument considerably. It enables the generation of very narrow size distribution even when a relatively high sample flow rate is needed, it enables measurements of size distributions in the range well below 1 nm with good size resolution, and it permits fast measurements of the size distribution with the time for a single scan being as low as 1 s.

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