Deliverable D3.11: Reference instruments for multi-wavelength absorption measurements

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Reference Instruments for multi-wavelength absorption measurements

1 Short description

In the reporting period, a laboratory reference setup for determining particle light absorption coefficients at three wavelengths was developed. The reference absorption is determined by the difference of particle light extinction and scattering coefficients (EMS=Extinction Minus Scattering). The main instruments of the setup are a multi-wavelength Integrating Nephelometer that measures the particle light scattering coefficient at three wavelengths and each of the three extinction cells the particle light extinction coefficient for a single wavelength. A series of laboratory tests have shown that the accuracy of individual instruments, when operated in accordance with the manufacture's user manual, is sufficient for measuring scattering or extinction coefficients, respectively. However, further steps are required to derive the particle light absorption coefficients. These step do not improve the accuracy of individual instruments, but rather minimize systematic differences between them. This led to the development of standard operating procedures for calibration, operation, data processing and quality assurance.

The reference absorption set-up is the backbone of ECAC calibration workshop and laboratory experiments for characterizing filter-based absorption photometers.

2 Methodology

2.1 Method (EMS)

The reference absorption setup is based on one of the first principles of optics, that the absorption coefficient is the difference between extinction and scattering coefficients.

$$\sigma_a = \sigma_e - \sigma_s$$

Particle light extinction and scattering coefficients are measured independently of each other. The method has advantages and disadvantages compares to other method, such as photoacoustic spectroscopy or filter-based photometers to determine the particle absorption coefficient.

Pros:

- Particle light scattering coefficients can be measured with Integrating Nephelometers. Integrating Nephelometers are well known instruments calibrated and traced back to SI units with two gases with known molecular scattering coefficients.
- The calibration of the extinction measurements can be bound to light scattering measurements using non-absorbing particles. This method is also suggested in the standard operating procedures for regular performance checks.
- The overall method is based on basic optical properties and is traceable to SI units.

Cons:

- The difference between values of extinction and scattering can have a high relative uncertainty. The reasons are systematic errors and noise. Both are significant when having small differences between extinction and scattering coefficients. This leads to a high detection limit.
- Thoroughly designed set-up and high experimental effort to avoid systematic errors. These include: (i) inlet systems to avoid particle transport losses, (ii) proper instrument corrections, and (iii) regular quality assurance.

2.2 Set-up

The set-up consists of an Ecotech Integration Nephelometer, type Aurora4000, with wavelengths of 450, 525 and 635 nm. The Integrating Nephelometer is operated in total and backscattering mode. The polar mode, which allows the measurement of particle light scattering in more than two sectors, is not used as this would reduce the temporal resolution. In order to ensure a constant aerosol flow, the Integrating Nephelometer detection cell is operated by an external pump instead of the internal blower. Two-point calibrations with particle-free air and CO_2 are performed manually by the instrument operator. In order to fill the chamber homogeneously with calibration gases, these gases are supplied via the aerosol inlet. Automatic zero measurements are carried out using a motorized three-way valve, which switches between aerosol and zero air.

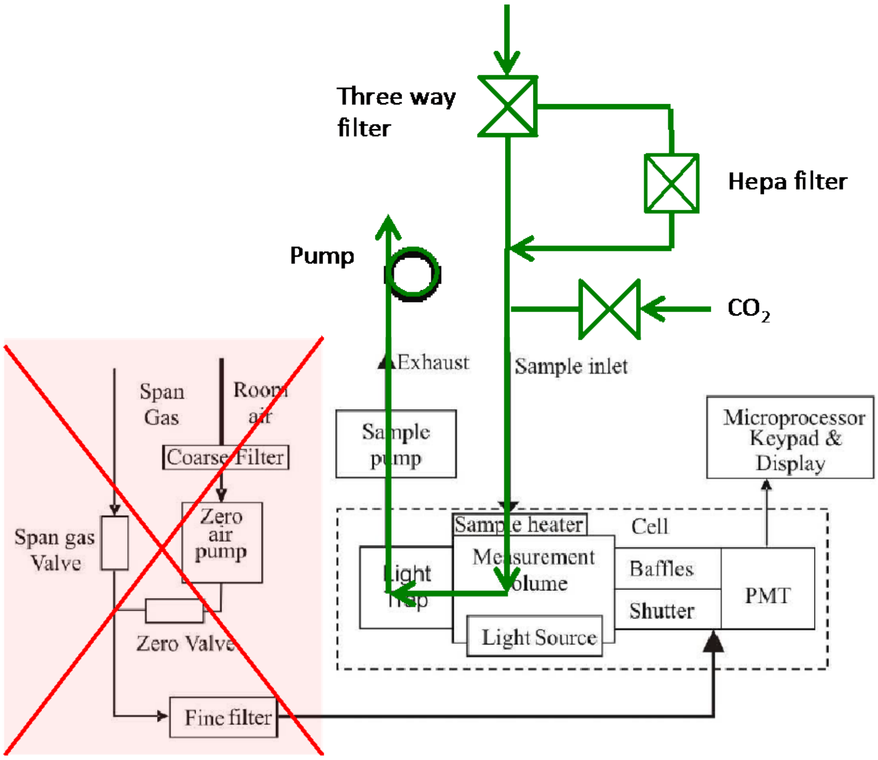

Figure 1: Modification of Aurora4000. Newly installed span gas and zero air unit (green) and disabled parts in the Nephelometer (red).

The three CAPS with wavelengths 450, 530 and 660 nm are operated without any modifications.

Nephelometer and CAPS are fed with the same aerosol via an aerosol splitter. The aerosol splitter is connected to a mixing chamber what can be filled with different aerosols (e.g. experiments with ammonium sulphate, CAST soot, ambient air and filtered air). The role of the mixing chamber is to provide the absorption reference and other instruments under test with the same aerosol. The large volume of 0.5 m^3 also works as a buffer for smoothing temporal fluctuations of aerosol concentration.

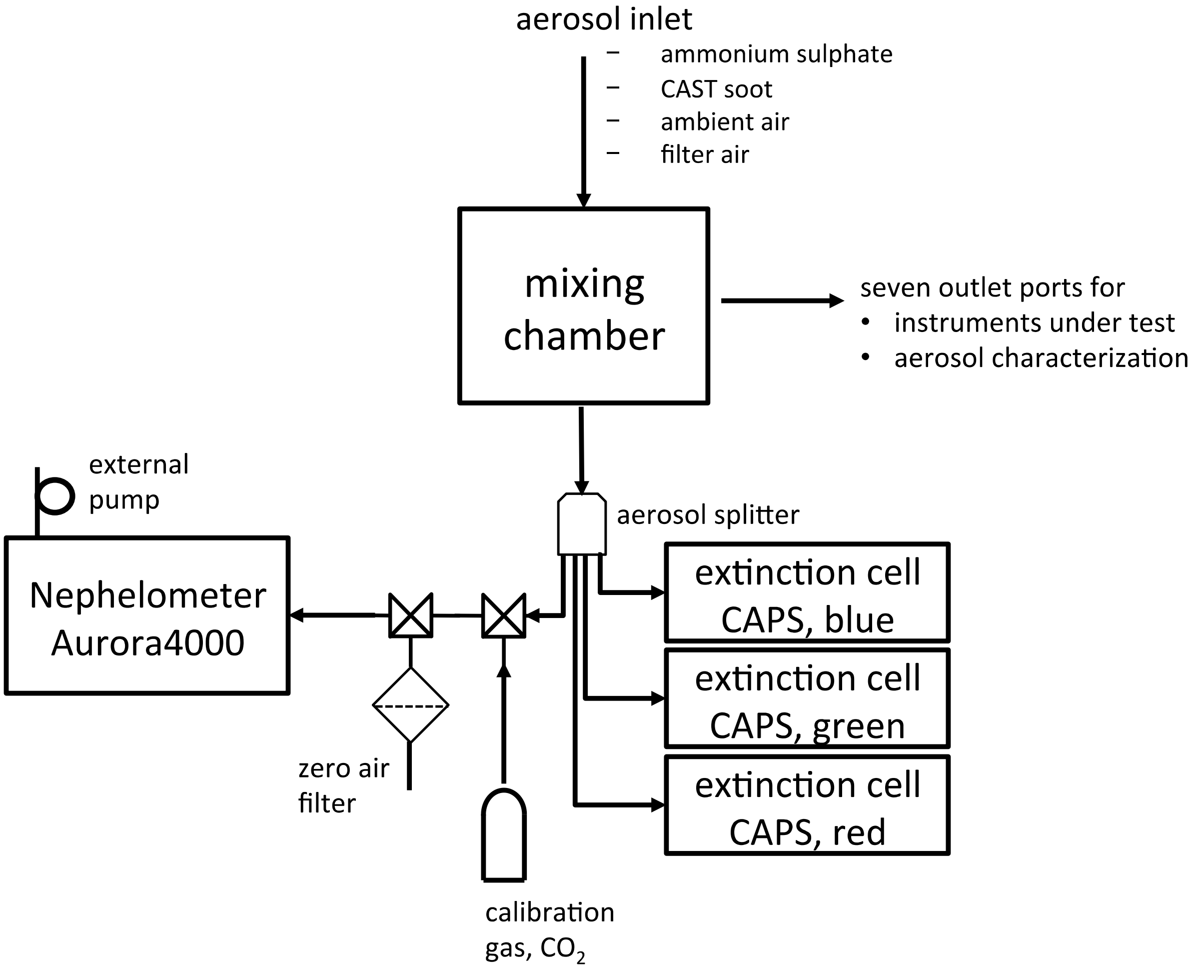

Figure 2: Schematic of absorption reference setup.

2.3 Calibration chain

There are two potential ways calibrating an Integrating Nephelometer and extinction cells.

The first way is to take the extinction cell as the primary instrument. Basically, extinction cells don't require a calibration as long as the path length is precisely know. This approach also is valid for cavity attenuated phase shift (CAPS) instrument. CAPS measures the particle light extinction coefficient in an optical multi-reflection cell. The mirrors at the cell ends are kept clean by a thin layer particle free air. This causes a dilution or an effective path length little shorter than the geometrical path length. Petzold et al. (2013) published a correction to the effective path length, what should allow to use CAPS as absolute reference. It was found later, that CAPS suffers from a non-linear response and also the effective path length correction factor may vary from instrument to instrument. For that reason, the primary idea of using CAPS as absolute reference was dropped.

Instead, the primary calibration is based on measuring the Rayleigh scattering of CO_2 and air with the Nephelometer. Rayleigh scattering coefficients of CO_2 and air are known (Anderson et al., 1996) with an uncertainty of 0.24% and 0.90%, respectively. The repeatability of a calibration of an Integrating Nephelometer with the same gas bottles yields an accuracy of about 3%. This value is the accepted uncertainty for Integrating Nephelometers at the green and blue wavelengths. For the red wavelength (λ>600 nm), the uncertainty larger with values of about 5%.

Integrating Nephelometers suffer from a geometric truncation of the light integrating unit and an imperfect illumination of the measurement cell. A correction for the so-called truncation error was published in Müller et al. (2011) for the Ecotech Integrating Nephelometer, type Aurora3000. The cell geometry and angular intensity distribution of Aurora4000 is the identical to the Aurora3000. Therefore, the truncation correction can be used for both instruments. The uncertainty of the correction is difficult to estimate, since corrections are based on light scattering calculation. It was shown by Bond et al. (2009), that systematic error of 1-5% occur for absorbing particles, when using this correction. Although the study of Bond et al. (2009) is for Integrating Nephelometers type TSI-3563, the results are valid also for the Aurora4000 Integrating Nephelometer.

In summary, an Integrating Nephelometer can be used as reference instrument to derive a calibration function for CAPS to compensate for effective path length and non-linearity artefacts.

Since the CAPS and Integrating Nephelometer operate at different wavelengths, an inter- extrapolation rule is applied. The wavelength dependences of particle light scattering and extinction coefficients are typically parameterised by the Ångström law

$$AE = \frac{-ln(\sigma_1/\sigma_2)}{-ln(\lambda_1/\lambda_2)},$$

whereas it is assumed that the Ångström exponent is constant over a large wavelength range. Errors due to wavelength inter- and extrapolation can be neglected compared to the uncertainty of the measured particle light scattering and extinction coefficients.

The CAPS calibration is performed by comparing the particle light extinction with the scattering coefficients from the Integrating Nephelometer, which is corrected for the truncation error. To minimize the truncation error correction, it is suggested to use ammonium sulfate, having a scattering Ångström exponent similar to that expected for the particle number size distribution, which later will by analysed. Since the scattering Ångström exponent of the ambient aerosol is variable, this method is merely a minimization of systematic errors.

The full calibration procedure of the reference set-up can be summarized as follows:

1. Full calibration of Aurora4000 with high and low span gas
2. Generation of ammonium sulfate with a proper scattering Ångström exponent with a large range of particle number concentrations.
3. Truncation error correction of the particle light scattering coefficient of the Integrating Nephelometer
4. Inter- and extrapolation of the particle light scattering coefficients to CAPS wavelengths
5. Derivation of the correction function for each CAPS from the comparison of particle light scattering and extinction coefficients.

2.4 CAPS specifications

Non-Linearity correction

A non-linearity between the measured particle light extinction and scattering coefficients was found due to a non-linearity in the CAPSs. The degree of non-linearity differs from CAPS to CAPS. A correction was derived from a comparison of particle light extinction coefficients to truncation-corrected particle light scattering coefficients, using non-absorbing particles, in this case ammonium sulfate particles.

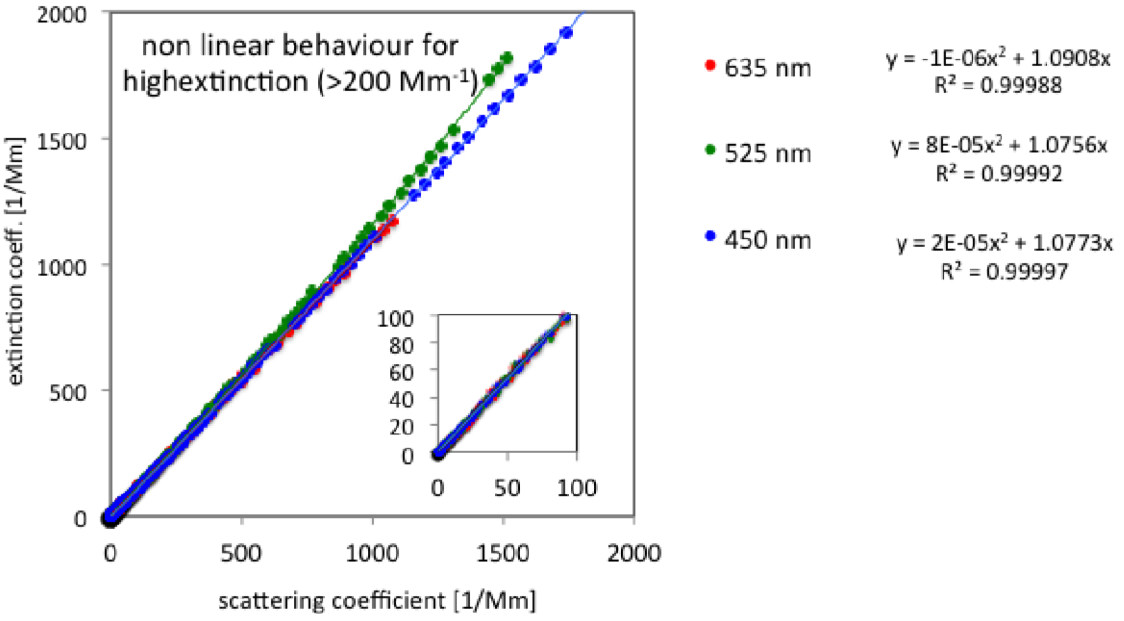

Figure 3: Non-linearity for the three CAPS.

Since the particle light absorption coefficient is determined from the difference of the particle light extinction and scattering coefficients, the uncertainty depends on the single scattering albedo and on the calibration uncertainties of the Integrating Nephelometer and the different CAPS. For soot, generated by a propane gas burner (miniCAST, Jing Ltd.) with low single scattering albedos (<0.2) and high extinction coefficients (>100 Mm^{-1}), the relative error has it's minimum value of 3%.

2.5 Integrating Nephelometer Specifications

Aurora 4000:

Manufacturer:	Ecotech Pty Ltd, Knoxfield, Australia
Wavelengths:	450, 525, 635 nm
Operating modes:	‘Polar mode’: Scattering of light in up to 18 angular ranges. The angular ranges 0°-180° and 90°-180° correspond to total and backscattering, respectively.
Truncation corrections:	Corrections using the Ångström scattering coefficient and based on Mie calculations are possible. Truncation correction for total and backscattering is the same as for Aurora3000 (c.f. Müller et al., 2011).

2.6 EMS specifications

Specifications for EMS result from calculations based on the specification of individual instruments. The uncertainty of minute samples of scattering and extinction coefficients are about 0.2 Mm^{-1}. The errors in the gas calibration of the Integrating Nephelometer and truncation correction are 3% and 2%, respectively.

Error propagation leads to the uncertainty for the derived particle light absorption coefficients. The uncertainty depends on many parameters and cannot be summarized easily in a table. Instead, the relative uncertainty of the particle light absorption coefficient is shown in Fig. 4. The relative error is

function of the particle number concentration, represented by the particle light extinction coefficient, and the single scattering albedo ω_0 (=σ_{sca}/ σ_{ext}). The curves can be explained as follows.
The minimum value of the relative error of about 3% follows from the uncertainty of the calibration of the Integrating Nephelometer. This value can be reach under two conditions. These are high concentration, so that the influence of instrumental noise is low. Furthermore, the single scattering albedo must be relative low that the difference between particle light extinction and scattering is large. Otherwise, systematic errors become significant. For the same reasons, the relative error is increasing for low concentrations and high single scattering albedos.

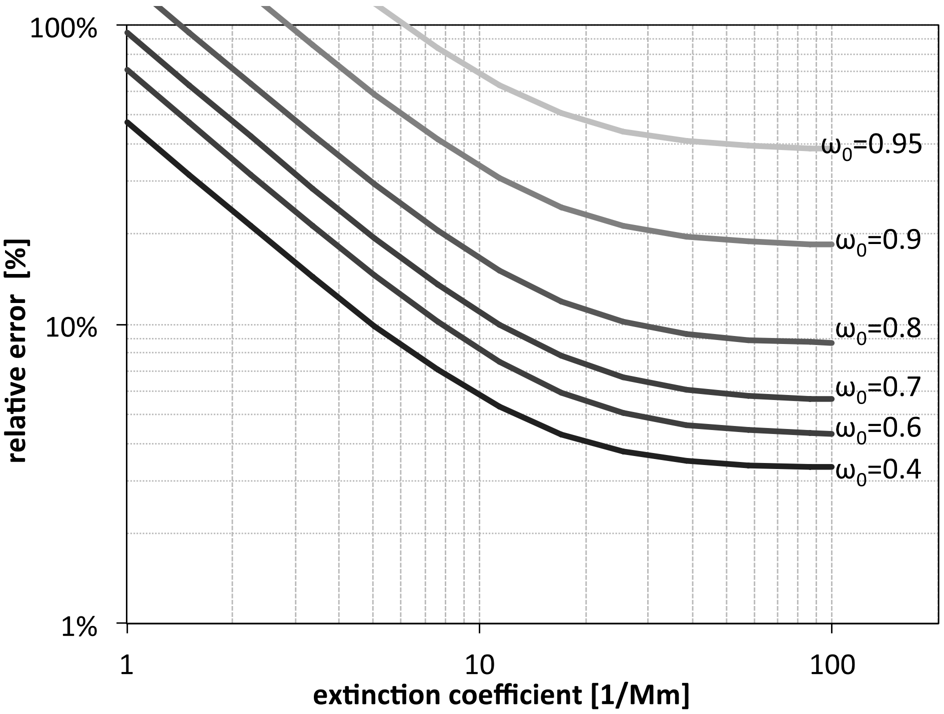

Figure 4: Relative uncertainty of the EMS absorption method as function of the particle light extinction coefficient and single scattering albedo.

The EMS method has some limitations. These are: i) The uncertainty is high in the case of low single scattering albedos, and (ii) the uncertainty is high at low concentrations. This limitation restricts the use for indoor air measurements.

3 Standard operating procedures

Standard operating procedures have been developed on basis of experience and known instruments artefacts and performance. The Standard operating procedures are split in three sections: calibration, measurement and data processing.

1 Calibration	
1.1 Integrating Nephelometer calibration	• The Integrating Nephelometer has to be calibrated according to the manufactures recommendation and suggested scattering cross sections for air and CO_2. • Alternatively, calibration constants are not applied, but considered in post processing.
1.2 CAPS calibration	• Generation of ammonium sulfate aerosol with low relative humidity (RH<30%). For deriving non-linear

	artefact the extinction coefficients should cover the range between 0 and 1000 Mm^{-1}. Other non-absorbing aerosol are desirable but were not tested. • Measuring of the particle light scattering and extinction coefficients with high temporal resolution (<10 s). • The Integrating Nephelometer has a larger cell than the CAPS, which results in a time constant and probably a time shift. Depending on the flow through the Integrating Nephelometer, the time shift must be corrected for. • Truncation error correction of the particle light scattering coefficients. It is important to note which method of truncation error correction is applied. • It is good practice to correct scattering and extinction coefficients to STP conditions (T_0=273 K, P_0=1013.25hPa). • Comparison of the particle light extinction with scattering coefficients. A second order polynomial function is sufficient to derive correction factors for the effective path-length and non-linearity.
1.3 Instrumental noise	• Record instrumental noise (single standard deviation) for the Integrating Nephelometer and CAPS by measuring the light scattering and extinction coefficients of particle-free air. Note: the background of CAPS is sensitive to pressure changes. Wait at least for one auto zero cycle or do a manual zero measurement.
1.4 Documentation of calibration results	• It is good practice to archive calibration results. These are: Integrating Nephelometer calibration factors, instrumental noise, truncation correction method, polynomial CAPS correction function, aerosol type, aerosol temperature, pressure and humidity.

2 Normal operation	
2.1 Instrumental noise and zero test	• Baseline level and instrumental noise are important for data quality. It is recommended to start experiments with a long zero period of about 30 minutes. Automatic zero measurements for CAPS are performed every 15 minutes. The Integrating Nephelometer baseline should be checked at least every 24 hours.
2.2 Switching between zero air and aerosol	• Since the CAPS reacts sensitively to pressure changes, data should be rejected until the next zero period.
2.2 Final zero check	• It is recommended to carry out a final zero check after the measuring task.

3 Data logging and processing	
3.1 Data logger	• It is recommended to capture data with a high temporal resolution of at least 10 seconds or faster. Time intervals of the CAPS and the Integrating Nephelometer should be synchronized. • If the time shift between instruments is significant, it must be corrected for.

3.2 Truncation correction	• The Integrating Nephelometer must be corrected for truncation errors, preferably using the same method used for calibration.
3.3 Temperature and pressure correction	• Data from all instruments must be corrected to standard temperature and pressure
3.4 Calculate absorption coefficients	• Interpolation of the particle light scattering and extinction coefficients to other wavelengths using the Ångström interpolation rule and to calculate the particle light absorption coefficients.

4 Quality assurance	
4.1 Short term stability	• The short-term stability is the stability of calibration constants over a period of several days. The baseline drift is not part of the short-term stability, as it is taken into account by regular baseline measurements. The short-term stability can be determined by repeated CO_2 and ammonium sulphate calibrations.
4.2 Long term stability	• The long-term stability treats drift of calibration constants over a period of one week to months. It is strongly recommended to monitor the long-term stability in order to identify a systematic drift.

Cross sensitivity to organics

Sometimes a severe drift in the background was observed. During a field study, this artefact occurred several times and was significant. It was found that the background drift is correlated with high number concentrations of ultrafine particles. Furthermore, the drift is larger for the shorter wavelengths. Fig. 5 shows the background versus the particle number concentration at 15.8 nm measured with a mobility particle size spectrometer. It was found that the correlation for this diameter is highest. Scattering and absorption cross-sections for ultrafine particles (d_p<100 nm) are too small to cause a background of up to 40 Mm^{-1}. It is speculated that the background drift is related to volatile particles, which could be collected and accumulated onto the zero filter and concurrently released into the gas phase. Laboratory measurements to support or to disprove this thesis are planned.

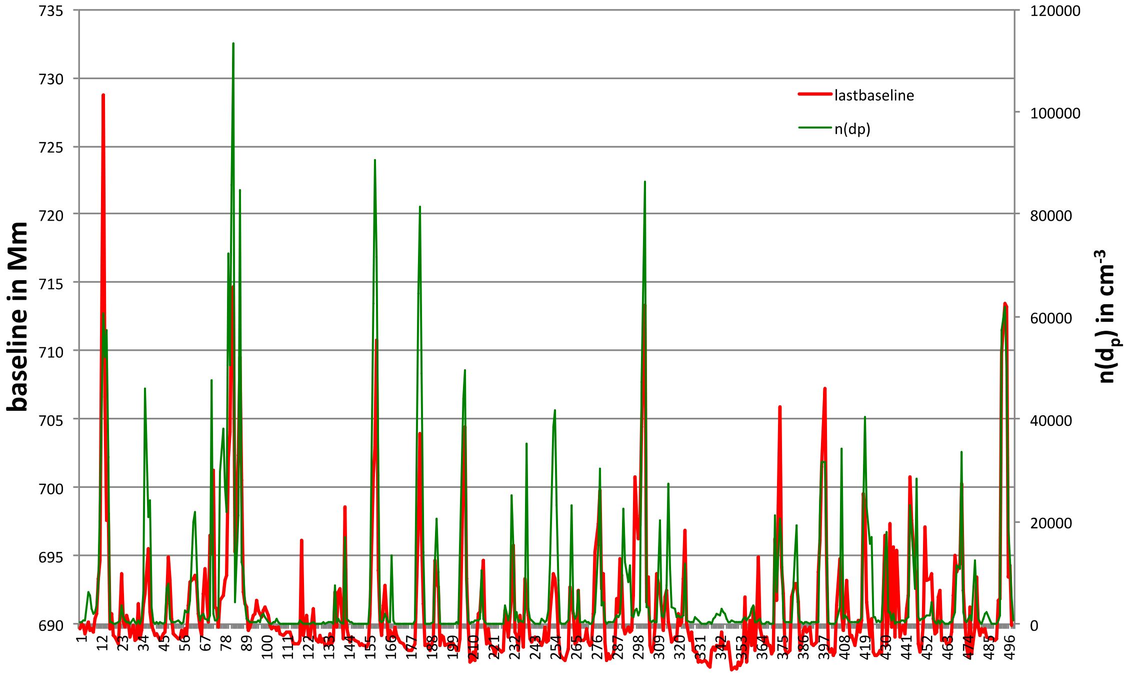

Figure 5: Series of baseline signals at 450 nm and concentration of ultrafine particles of size 15.8 nm.

Until this problem is solved, laboratory measurements with the EMS reference should only be carried out with aerosols with a low OC content.

4 Summary

The EMS method is a primary method for measuring the particle light absorption coefficient. The method can be calibrated with methods known in aerosol technology without the need for an aerosol calibration standard. The coupling of two known techniques, particle light and extinction measurements require a careful experimental work to prevent systematic errors.

The method is subject to certain limitations in terms of detection limit and aerosol type. The method can only be used to a limited extent for measurements of the particle light absorption coefficient of the ambient aerosol. The strengthening of the method lies in the characterization of laboratory-generated aerosols or in the use as primary standard for particle light absorption to calibrate other techniques.

References

Anderson, T. L., et al. (1996). "Performance characteristics of a high-sensitivity, three-wavelength, total scatter/backscatter nephelometer." Journal of Atmospheric and Oceanic Technology 13(5): 967-986.

Bond, T. C., et al. (2009). "Truncation and Angular-Scattering Corrections for Absorbing Aerosol in the TSI 3563 Nephelometer." Aerosol Science and Technology 43(9): 866-871.

Müller, T., et al. (2011). "Design and performance of a three-wavelength LED-based total scatter and backscatter integrating nephelometer." Atmospheric Measurement Techniques 4: 1291-1303.

Petzold, A., et al. (2013). "Intercomparison of a Cavity Attenuated Phase Shift-based extinction monitor (CAPS PMex) with an integrating nephelometer and a filter-based absorption monitor." Atmospheric Measurement Techniques 6(5): 1141-1151.